ENGINEERING BIOBASED INTERPENETRATING POLYMER NETWORKS BASED ON PLANT (SOYBEAN) OIL AND POLYSILOXANES

By

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ABSTRACT

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Interpenetrating Polymer Networks (IPNs) are materials containing two or more immiscible components that have been polymerized and crosslinked in the presence of each other to form entangled (interpenetrated) networks. The intimate mixing of such crosslinked entangled networks results in a single-phase morphology on the macro scale and leads to interesting physical properties that are different than those of the individual polymeric components. Currently, products derived from IPNs find a wide range of applications in the industry. Of particular interest here are IPNs derived from polysiloxanes with rigid polymers such as polyacrylates or polystyrene, where the silicone phase provides high flexibility, water vapor permeability and biocompatibility.

This thesis reports on studies of newly engineered biobased IPN systems based on soybean oil and polysiloxanes. The soybean oil was silylated with vinyltrimethoxy silane via the "ene reaction" chemistry to provide the necessary crosslink sites. Similarly, oligomerized soybean oil was silylated and was used to provide a more viscous, higher molecular weight oil for the IPN formation. The second component in these IPNs was either a silanol terminated polydimethylsiloxane (PDMS) or carbinol containing hydrophilic polysiloxanes. High molecular weight PDMS was prepared by emulsion polymerization of silanol terminated dimethylsiloxane oligomers. Carbinol containing hydrophilic polysiloxanes were prepared by polymerization of 3-aminopropylmethyldiethoxysilane followed by a reaction of the amines with cyclic carbonate.

These hydrophilic polysiloxanes were water-soluble independent of the water pH or their molecular weight and were characterized by high degree of hydrogen bonding.

A series of IPNs were prepared containing different concentrations of silylated soybean oil and silicone polymers. Different processing methods (e.g. a latex method and a solution method) were studied and IPNs were formed by the evaporation of the water or the solvent led to stable siloxane crosslinks. Another process involved IPNs prepared by dissolving the water soluble polysiloxanes in the water phase that was used to emulsify the silylated soybean oil.

The siloxane crosslinks control the morphology and prevents gross phase separation of the soybean oil phase and the silicone phase. A model, based on Donatelli's equation was constructed to determine the crosslink density of these networks, which was then correlated with the physical properties of these IPNs. The morphology of cast films from each of these IPNs revealed an intimate mixing of the two immiscible components with no apparent gross phase separation. The crosslink density, mechanical properties, thermal properties and surface properties of all IPNs were investigated and correlated with their composition.

These IPNs can be utilized as high release liners, low friction materials or as general protective coatings. The combination of natural product with polysiloxanes makes these IPNs also suitable for various applications in cosmetics and personal care. The IPNs containing the hydrolytically susceptible siloxy crosslinks can be utilized to prepare environmentally degradable materials that can be utilized in various control release applications.

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KEY TO ABBREVIATIONS

Full Name	Abbreviations/ Symbol
Interpenetrating Polymer Networks	IPNs
Thermo-gravimetric Analysis	TGA
Gel Permeation Chromatography	GPC
Differential Scanning Calorimetry	DSC
Weight average molecular weight	Mw
Number average molecular weight	Mn
Polydispersity index	PDI
Glass transition temperature	Tg
Polystyrene	PS
Tetrahydrofuran	THF
Design of Experiments	DoE
Hexamethyldisiloxanes	HMDSO
Dynamic Mechanical Analysis	DMA
Ethylene carbonate	EC
3-aminopropyldiethoxymethylsilane	APDES
Scanning Electron Microscope	SEM
Nuclear Magnetic Resonance Spectroscopy	NMR
Fourier Transform Infrared Spectroscopy	FTIR

CHAPTER 1: INTRODUCTION, BACKGROUND AND OUTLINE OF THE DISSERTATION

1.1. INTRODUCTION

Polymers are an important class of materials, which are found in a variety of applications from drug delivery to solar cells and from highly rigid structural polymers to very thin and flexible coatings. A single polymer cannot fulfill all the applications and thus multicomponent polymeric systems such as copolymers, polymer blends and composites have received a considerable interest for a long time. One of the recent terms in the array of multicomponent polymer systems is the interpenetrating polymer network (IPN), which was first introduced in the 1960s by John Millar [1].

By definition, an IPN is a material containing two or more components that have been polymerized and vulcanized (crosslinked) in the presence of each other to form entangled networks (interpenetrated) with each other [2]. Thus, the morphology of an IPN is different from that of any grafted copolymer or a simple blend of two polymers. It was found that the morphology of such intimate entanglements of two, or more, immiscible polymeric networks can lead to interesting physical properties that cannot be achieved by grafting, blending or other mixing techniques. This is because, in these techniques, the immiscible polymers tend to phaseseparate, leading to two or more distinct phases that show a non-uniform structure and hence inferior properties. On the other hand, the IPN has single-phase morphology with no phase separation at the macro scale. Currently, products derived from IPNs find applications ranging from false teeth to ion-exchange resins, adhesives, high impact plastics, thermoplastics, vibration-damping materials (for outdoor, aircraft and machinery applications), high temperature alloys and medical devices [3]. Table 1 lists some IPNs that are available commercially[2]. In this report, we will discuss the various IPNs derived from biobased materials as well as from polydimethylsiloxane, their properties and applications and a method devised to combine these two systems for the synthesis of a new IPN, which can be used for coating applications.

MANUFACTURER	TRADE NAME	COMPOSITION	APPLICATION
Shell Chemical Co.	Kraton IPN	SEBS-Polyester	Automotive Parts
LNP Plastics	Rimplast	Silicone Rubbers-Nylon or PU	Gears or Medical
ICI Americas Inc.	ITP	PU-polyester-styrene	Sheet Molding Compound
DSM N.V.	Kelburon	PP-EP or Rubber-PE	Automotive Parts
Shell Research B.V.		Rubber-PP	Tough Plastic
Uniroyal (Reichhold Chemical Co.)	TPR	EPDM-PP	Auto Bumper Parts
Sun Marketing and Refining Co.	-	PE-PP	Low Temperature Plastics
Rohm & Haas	-	Anionic-Cationic	Ion-Exchange Resins
Advanced Elastomer Systems	Santoprene	EPDM-PP	Tires, Hoses, Belts and Gaskets
Du Pont	Somel	EPDM-PP	Outdoor Weathering
BF Goodrich	Telcar	EPDM-PP or PE	Tubing, liners and wire and cable insulation
Allied Chemical	ET Polymer	Butyl Rubber-PE	Sheet Molding Compounds
Hercules	Profax	EPDM-PP	Ultrahigh Impact Resistance
Exxon	Vistalon	EPDM-PP	Paintable Automotive Parts
Freeman Chemical	Acpol	Acrylic-urethane-polystyrene	Sheet Molding Compounds.
Dentsply International	Trubyte, Bioform	Acryl-based	Artificial Teeth
Hitachi Chemical		Vinyl-Phenolics	Damping Compounds
BioMed Sciences	Silon	PDMS-PFTE	Medical Dressing

 Table 1. 1 Examples of some commercial IPNs [2]

1.2. BACKGROUND

Petrochemicals have revolutionized the chemical industry in many ways by generating fuels required by industrial growth as well as by generating chemicals that can be used for day-to-day applications ranging from food additives to furniture, textile materials etc. The plastics and polymer industries are examples of petroleum based industries with a yearly production of about 300 million tons [4, 5].

The major disadvantage of using petrochemical based resources is the non-sustainability of the process [6]. Fossils take about a million years to form, while it takes about 1-10 years to extract the fossils, process them chemically to prepare several chemicals, polymers and fuels. The end-of-life for these polymers is the carbon dioxide released in the atmosphere. This carbon dioxide is fixed by plants using photosynthesis for their growth. The plants and vegetation, after millions of years of degradation form fossil fuels. Thus, the conversion of biomass to plants is a longer process than the use of these fossils and this step makes the whole process nonsustainable [7].

Bio-based products, which are directly derived from biomass such as wood, cotton, oils and leather, can make the process sustainable by eliminating the use of petroleum based resources [7, 8]. Hence the incorporation of biobased materials into the current products is a need for tomorrow. Currently, about 1% of the total polymers made globally are made from biobased materials and several programs such as "Bio-preferred[®]" are promoting the development, purchase and use of biobased products in United States [9].

The biobased and bio-renewable carbon feedstock from plants by chemical processes mainly come from two resources – polysaccharide base and vegetable oil base[5-8]. The polysaccharide based feedstock contains biopolymers such as starches or cellulosics, while the vegetable oil based feedstock incorporates triglycerides of fatty acids containing C-9 to C-18 platform. Both of these have been extensively explored and used in the formation of IPNs.

1.2.1. Biobased IPNs

Among triglycerides, several biobased oils have been incorporated into IPNs due to the availability of the crosslinkable functional groups on their backbone. Castor oil has been studied extensively for the formation of polyesters and epoxies because of the hydroxyl functional groups present in the chain (See Figure 1.1).

IPNs of castor oil triglycerides with poly (ethylene terephthalate) (PET) that were prepared by ester-ester as well as ester-hydroxyl interchange reactions exhibited a higher degree of toughness and faster crystallization rates than PET alone [10] This might be the result of a hybrid semi-IPN structure formed between the two phases consisting of a copolymer of castor oil and PET. It was found that the change in the rate of crystallization was due to the "oil characteristics"[10]. Plasticization and nucleation occurred at the crosslinks in the oil present. IPNs prepared from castor oil-based polyurethanes and styrene monomers by the simultaneous method of synthesis were reported to be tough elastomers or reinforced plastics, depending on their composition and hence the two phase morphology, which was directly related to reaction time, process time and crosslinking [11, 12]. IPNs based on castor oil polyurethanes (PU) with acrylics were elastomeric and exhibited good mechanical properties [13-15] especially toughness and fracture resistance. In the IPN made from castor oil based PU and poly (methyl acrylate), low chemical resistance for solvents was observed while the light transmittance was higher. The IPNs made from castor oil based polyester and poly (methyl methacrylate) showed poor mechanical properties due to the phase separation which was observed from DSC analysis [16]. This establishes the fact that IPN homogeneity plays an important role in achieving the targeted properties.



Figure 1. 1Structure of castor oil (Triricinolein)

Many other IPNs have also been prepared from functionalized triglycerides of Vernonia using the epoxide backbone of the oil as a functional group that can be utilized for polymerization [17] (Figure 1.2). It has been reported that the IPN synthesized using polyesters from vernonia oil showed lower glass transition temperatures than that of castor oil [17].



Figure 1. 2Structure of vernonia oil (Trivernolin)

A triglyceride derived from *Lesquerellapalmeri*, a plant native to Arizona and Northern Mexico, has also been used to synthesize IPNs. The oil from this plant has hydroxyl groups like castor oil, but the acid residue of the oil has two more methylene groups (Figure 1.3). The polyester IPNs produce lower glass transition temperature (T_g) than castor oil and epoxides give slightly higher glass transition temperature but giving more control of the reaction[18]. Simultaneous Interpenetrating Networks (SIN) and sequential IPNs formed from *Lesquerellapalmeri* and polystyrene yield tougher IPNs with higher energy of elongation than polystyrene (PS)[19].



Figure 1. 3Structure of *Lesquerellapalmeri* oil (Trilesquerolic acid)

Crambe and linseed oil (as well as their epoxidized derivatives) have also been studied by forming IPNs with polystyrene and polyacrylics[20-22]. A recent comprehensive review of natural oils and synthetic polymers is also available explaining their contribution in IPN [23].

Most of the previous IPN work with triglycerides either involved preparing homogeneous solutions of the triglycerides and the monomer and then polymerizing and crosslinking as phase separation occurs or polymerizing them as an epoxy or polyester polymer and then forming an IPN with some rigid polymer like PS to combine the properties. The morphology of the resulting IPN was a function of the kinetics of the phase separation.

1.2.1.1.1. Soybean Oil

Soybean is one of the largest commodity crops in the world. It is also starting to play a major role in reducing carbon footprints and replacing nonrenewable resources such as fossil fuels. According to USDA's World Agricultural Supply and Demand Estimates (WASDE) report, the United States is the largest producer and exporter of soybeans in the world with estimated production in 2013/ 2014 to be 3289 million bushels producing around 20,000 million pounds of soybean oil per year [24]. Soybean is the second largest crop in Michigan with about two million acres grown each year, and the commodity adds approximately \$1 billion to the state's economy.

Soybean oil, on average, contains about 15% saturated fatty acids per mole of triglyceride, while it has about 4.6 double bonds/ mole. However, soybean oil does not contain any crosslinkable functional group in the backbone of the triglyceride.

A typical triglyceride of soybean contains a variety of fatty acids as shown in the Table 1.2.

Fatty Acid	Structure	%
Palmitic Acid	مىمىمىمىڭ مىر	7 -11
Stearic Acid		2 - 6
Oleic Acid		22 - 34
Linoleic Acid		43 - 56
Linolenic Acid	, OH	5 - 11

Table 1. 2 Typical composition of fatty acids found in soybean oil

1.2.2. IPNs Containing Polydimethylsiloxane (PDMS)

PDMS has some unusual properties that can be used to prepare unique IPNs. As a polymer, PDMS is easy to synthesize and can offer a variety of functional groups as compared to other silicon polymers. It has a glass transition temperature of -125°C and it is very flexible. It is highly water resistant but is highly permeable to water vapor. However, PDMS does not have a high modulus and thus it has to be reinforced with silica in order to improve its mechanical properties. Its hydrophobicity can be a drawback [25] for certain targeted applications. Thus, the synthesis of IPNs derived from PDMS and rigid polymers such as polystyrene or a polyacrylate have been reviewed widely in the literature [20-33].

One of the methods for synthesis of an IPN containing PDMS is to form sequential IPNs with other organic polymers such as polyacrylates. When polymethacrylic acid was used in the IPN together with PDMS, phase separation was observed with domains of polymethacrylic acid in the PDMS polymer [26]. This is termed "sea-island morphology", where a second polymer forms small domains that are dispersed in the network of the first polymer. This morphology is characteristic of PDMS IPNs, which indicates the permeability of the material. On the contrary,

the other morphology consists of co-continuous phases in which the concentration of the first polymer is higher and the second polymer forms small domains that are connected to each other, which makes the polymer impermeable. Poly (2-hydroxyethyl methacrylate) has also been extensively studied to form IPNs with PDMS due to its potential in biomedical applications [27-33]. The tensile strength of the material improved, but the hardness of the IPN was lower than the original material. SIPN of PDMS and polystyrene was prepared targeting the permeability and selectivity of each polymer [34]. This IPN was designed for separation of aqueous ethanol owing to selective permeability of PDMS for water and that of polystyrene to ethanol. The permeation properties obtained were similar to that of PS, but the mechanical properties were better than PS, thus extending the life of the membrane. Similarly, a SIPN was formed from vinyl terminated PDMS and aromatic polyimide for methanol/toluene azeotrope separation by pervaporation[35]. The newly formed membrane reduced the water vapor diffusion rate significantly, indicating the altered properties of the IPN compared with polyimide alone. Together with mechanical properties, the toluene permeation and membrane selectivity were all improved to give a better overall performance. IPN of PDMS with epoxy was also made by semi-sequential and semi-simultaneous method by mixing partially crosslinked PDMS with diglycidylether of bisphenol-A (DGEBPA) and a curing catalyst. Thus, curing occurred simultaneously as well as separately[36]. Partial crosslinking and silica addition before curing reduced the phase separation due to hydrogen bonding of silica. The resulting material formed showed better ductility and toughness than the parent polymers. Polyurethane methacrylate (PUMA)-silicon IPN was synthesized by UV crosslinking of PUMA and γmethacryloxypropyltrimethoxy silane (γ -MPS) as a crosslinking agent for PDMS[37] condensing silica. For the same material, a thermal crosslinking method was also used. The results indicate that the thermal properties are improved for PUMA while the surface hardness and glass transition temperature of the IPN is lower than the reactants. It has been noted in the literature that the improvements in thermal properties can be attributed to the presence of silica in the IPN. In the synthesis of IPN using castor oil based polyurethane and PDMS in the presence of a compatibilizer at various proportions[38], it was observed that the IPN has better thermal stability if the PDMS proportion in it is increased. The rigidity, as expected, was also a function of PDMS concentration in the IPN. The IPN however showed a highly heterogeneous nature making the two polymers incompatible with each other. Thus, it is important to have homogeneous morphology of IPNs to obtain improved properties.

The technique for obtaining a homogeneous morphology for IPN has three parameters; mixing of the two components, chain mobility of two polymers and the extent of crosslinking[25]. Mixing is important to obtain a uniform distribution of both polymers, which is also related to the compatibility of the two polymers. Chain mobility can be monitored by glass transition temperature of individual components. Higher chain mobility indicates a lower rate of crosslinking and thus lowers entanglement. Also, a lower rate of crosslinking can cause the phase separation as observed in the IPN formed between castor oil PU and PDMS[38]. The extent of crosslinking determines the stability of network and thus high crosslinking density ensures more entanglement. These are the issues especially in the case of PDMS since it has a very low T_g compared with other organic polymers.

One of the methods to address this problem is the synthesis of IPN using the latex method. A semi IPN of poly (tetrafluoroethylene) (PTFE) and poly (siloxane) was formed using the latex method. The resulting IPN showed higher thermal stability than PDMS alone and the thermal stability was increased as a direct function of the PTFE composition[39]. The T_g analysis

of the IPN confirmed that the increment in T_g is due to the entrapped fractions of PTFE in the siloxane network. The same method is used in the patents filed for the IPNs containing PDMS-PU, polyacrylate and poly (urethane-urea) [25] and semi-IPN containing PDMS-Polyamide [25, 40].

There are numerous IPNs containing polydimethyl siloxanes (PDMS) with a variety of synthetic polymers [23-33] showing microphase separation and multiphase structures due to the inherent immiscibility of PDMS with most organic polymers. Many of these IPNs have interesting and useful properties due to their high chain flexibility, low surface tension, high thermal stability and low T_g of the siloxane chain. Although there are large numbers of silicone containing IPNs, no IPNs of silicone polymers and soy triglyceride oils are described in the literature.

1.3. RESEARCH OBJECTIVE AND ORGANIZATION OF THE DISSERTATION

As mentioned in the background, IPNs derived from polysiloxanes and soy triglyceride oil have not been previously reported. This might be due to the absence of functional groups in soy triglycerides that can be used to crosslink them with PDMS and the tendency of the oil to phase separate from the polysiloxane.

In this work, biobased IPNs based on modified soy-triglycerides and polysiloxanes have been developed. The overview of the work presented in this thesis is given in figure 1.5.



Figure 1. 4 Schematic overview of the dissertation.

This thesis consists of six chapters and three major segments. The first segment (chapter 1) gives a general introduction of Interpenetrating Polymer Networks (IPNs), biobased materials and IPNs containing biobased materials and polysiloxanes.

The second segment involves developing a semi-empirical model to determine the crosslink density of the IPNs prepared. The crosslink density of the material plays an important role in determining the thermal and mechanical properties of the materials. Even though there are several methods to determine the crosslink density of the polymeric substances, the determination of crosslink density of IPNs has always been empirical. The chapter describes a model developed for the determination of crosslink density of the biobased IPNs developed in this dissertation based on their morphology.

The third segment (chapters 3-5) involves development of biobased IPNs from modified soybean oil and polysiloxanes. In chapter 3, a series of interpenetrating polymer networks (IPNs) was prepared using various concentrations of silylated soybean oil and PDMS that were cross linked with inorganic silicates. This series of IPNs was prepared from emulsions of silylated soybean oil and PDMS together with colloidal silica and dioctyltindilaurate catalyst at pH 10. Under these conditions, water soluble silicates reacted with silanols in the oil phase and formed intraparticle siloxane crosslinks. Upon casting films and evaporation of the water, additional interparticle cross linking were obtained between the coagulating particles to produce entangled networks of soybean oil and PDMS that were further reinforced by fine silica particles. The morphology revealed intimate mixing of the two immiscible components. The mechanical properties depended on the ratio of the soft, flexible PDMS phase and the rigid, brittle cross linked silylated soybean oil phase. These IPNs can be used as high release liners, low friction materials, or as a general protective coating.

In chapter 4, a series of interpenetrating polymer networks (IPNs) with different compositions were prepared from silylated oligomerized soybean oil (SOSO) and silanol terminated PDMS. Oligomerization of soybean oil was achieved by heating it with a catalyst in a Parr reactor at elevated temperatures. Vinyltrimethoxysilane (VTMS) was then grafted onto the oligomerized oil. Crosslinked films were obtained from solutions as the silanol groups between the two immiscible polymers condensed to form stable siloxanes linkages resulting in an entangled network characterized by microphase separation typical to IPNs. The crosslink density between the dispersed phase and the continuous phase was calculated from the average particle size of the dispersed phase. The mechanical and thermal properties were also studied and were directly related to the composition and the crosslink density. These IPN resins can be used

as high release liners, low friction materials, soft-feel coatings or as convenient one-package protective coatings.

In chapter 5, a series of IPNs with different compositions was prepared from emulsions of silvlated soybean oil (SilSoy) and hydrophilic polysiloxanes (HPPS). Silvlation of the soybean oil was achieved via the "Ene reaction" and the water soluble polysiloxanes were prepared by hydrolysis and condensation polymerization of 3-aminopropyldiethoxymethylsilane followed by a reaction with ethylene carbonate. Unlike the triglyceride structure of SilSoy, HPPS are water soluble, linear polysiloxanes with a pendent hydroxyl group on every siloxane. Evaporation of the water phase from emulsions of SilSoy in aqueous solutions of HPPS yielded crosslinked IPN films composed of silanols and carbinol condensations that formed stable siloxanes crosslink linkages as well as hydrolysable Si-O-C linkages. The entangled network that was obtained is characterized by intimate mixing of these incompatible phases with a typical IPN microphase separation. The crosslink density between the dispersed phase and the continuous phase was calculated from the average particle size of the dispersed phase and compared with swell-gel data. The mechanical and thermal properties were also studied and correlated with the composition and the crosslink density. These IPNs can be used as convenient environmentally degradable controlled release systems via the hydrolysis of the Si-O-C linkages.

CHAPTER 2: DEVELOPMENT OF A MODEL FOR PREDICTING CROSSLINK DENSITY OF THE IPNS BASED ON MODIFIED SOYBEAN OIL AND POLYSILOXANES

2.1. INTRODUCTION

The crosslinking between polymer chains is very important in controlling several polymer properties. Higher crosslinking density imparts higher glass transition temperature, higher modulus thus increasing the rigidity of the amorphous polymers. The covalent bonding between the two chains of the polymer reduces free chain movement and also reduces elongation of the polymer [41]. However, in case of elastomers, crosslinking is the essential parameter that stops the "slipping" of polymer chains across each other to impart elasticity.

The crosslinking of the polymers has been studied extensively in the literature. For the homogeneous polymers, there are several models that predict the polymer behavior mechanically as well as thermodynamically in terms of crosslinking. Some conventional methods for determining the crosslink density of polymer include modulus measurement and swelling behavior [42]. The determination of crosslink density from the modulus behavior is derived using statistical mechanics is given by the Mooney – Rivline equation based on the assumption that at constant temperature and volume, the elasticity of the polymer is entropically controlled [43, 44]. This system is convenient for homopolymers or for the single phase morphology since the surface energies between multiphase systems is not accounted for in the equation.

In case of IPNs, they inherently consist of dual phase morphology and hence the swelling methods are usually employed for the determination of crosslink density of IPNs. The molecular weight between crosslinks for the polymer or resin is calculated using Flory-Rehner equation incorporating the solubility parameter of the polymer for the selected solvent system [45]. This system is convenient for most of the polymers irrespective of their morphology provided the solubility parameter for the selected polymer-solvent pair is known. However, if the solubility parameter is not available for the system, then this method cannot be used for the determination of crosslink density.

Generally, the swelling behavior of the polymer in a suitable solvent is reflected in the crosslinking density of the polymer. This is a very convenient but empirical method to determine the crosslinking density of an IPN. It has been reported in the literature that the crosslinking density is inversely proportional to the swelling of an IPN, thus showing a trend in the crosslink density in terms of swelling behavior [46, 47]. However, this method only shows a trend in the crosslink density (usually with composition) and thus, it is not possible to compare the absolute value with any other systems.

Several attempts have been made to predict the crosslinking density of the IPNs based on the morphology of the polymer system since the morphology resembles the interaction between the two polymer phases [48]. It is very convenient to predict the crosslinking density from the morphology due to several reasons:

1. Morphology of IPNs actually resembles the phase interactions between the two phases, which is very important in case of IPNs.

2. Crosslinking density of the two polymeric systems in IPNs is also related to the composition of crosslinkable phase in an IPN, which could reflect in the morphology.

3. The compatibility of the two phases reflects in the crosslinking between them. This can easily be observed in the morphology of the system.

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Thus, it is faster, more convenient and less destructive method to determine crosslink density based on the morphology of the IPN.

2.2. MODEL DEVELOPMENT

Donatelliet. al. used a thermodynamic approach to derive a cellular domain size of the dispersed phase in an IPN [49]. In this chapter, we propose a model based on the Donatelli equation to calculate the crosslinking density of the IPNs prepared with different compositions of modified soybean oil and polysiloxanes. The Donatelli equation is given as -

$$\left(\frac{n_A \times D_B^3}{K^2 C^2}\right) \times \left(\frac{n_A}{1 - W_B} + \frac{2}{M_A}\right) + \left(\frac{W_B}{M_B} - \frac{n_A}{2}\right) D_B = \frac{2\gamma W_B}{RT}$$

Where,

 D_B : Diameter of the dispersed phase (Polymer B) in nm

 M_A : Molecular weight of polymer A

M_B: Molecular weight of polymer B

R: Gas constant in J/mole..K

T: Temperature in K

 γ : Interfacial energy between the two phases in dynes/cm

W_B: Weight fraction of the dispersed phase

 n_A : Crosslinking density of polymer A in moles/cm³

C: Proportionality constant relating the distance between the crosslink sites on polymer A and the domains of polymer B.

K: Flory's constant that relates Root Mean Square distances of swollen and unswollen particles with the average molecular weight

Now, by the definitions,

$$D_B = C \times r_A$$

Thus,

$$C^2 = \frac{D_B^2}{r_A^2}$$

Also, another substitution is,

 $r_o = K \times M^{1/2}$

In our case, $M = M_{EL}$, which is the segmental average molecular weight between crosslinks in polymer A [50].

Thus,

$$K^2 = \frac{r_0^2}{M_{EL}}$$

And

$$M_{EL} = \frac{W_A}{n_A}$$

Substituting these two equations into Donatelli equation, we get,

$$\left(\frac{n_A \times D_B^3}{\frac{r_0^2}{M_{EL}} \times \frac{D_B^2}{r_A^2}}\right) \times \left(\frac{n_A}{1 - W_B} + \frac{2}{M_A}\right) + \left(\frac{W_B}{M_B} - \frac{n_A}{2}\right) D_B = \frac{2\gamma W_B}{RT}$$

That is,

$$\left(\frac{n_A \times D_B}{\frac{n_A}{W_A} \times \frac{r_0^2}{r_A^2}}\right) \times \left(\frac{n_A}{1 - W_B} + \frac{2}{M_A}\right) + \left(\frac{W_B}{M_B} - \frac{n_A}{2}\right) D_B = \frac{2\gamma W_B}{RT}$$

Let the volume fraction of polymer A be V_A and that of polymer B be V_B .

Thus,

 $V_A + V_B = 1$

Now, while deriving the Donatelli equation, another term used was a_A , a linear deformation ratio for polymer A [51].

Thus,

$$a_A = \frac{r_A}{r_0} = V_A^{-\frac{1}{3}}$$

r and r_o are root mean square distances of swollen and unswollen molecules in polymer A.

Assuming the densities of both networks/ polymers to be the same, which is in correlation with the assumptions made in the cited literature (Also, density of PDMS is 0.965 gm/cm^3 and the density of SilSoy used is 0.945 gm/cm^3), we get,

 $\rho_A = \rho_B = 1 \, gm/cm^3$

Thus,

$$\frac{W_A}{V_A} = \frac{W_B}{V_B}$$

On solving further, we get,

$$\frac{W_A + W_B}{W_A} = \frac{V_A + V_B}{V_A}$$

Thus,

$$\frac{W_A + W_B}{W_A} = \frac{1}{V_A} = a_A^3$$

Also, since densities for the both polymers are the same,

 $W_A + W_B = 1$

Substituting these equations, we get,

$$\left(\frac{W_A \times D_B}{\frac{1}{a_A^{2/3}}}\right) \times \left(\frac{n_A}{1 - W_B} + \frac{2}{M_A}\right) + \left(\frac{W_B}{M_B} - \frac{n_A}{2}\right) D_B = \frac{2\gamma W_B}{RT}$$

$$\left(\frac{W_A \times D_B}{W_A^{2/3}}\right) \times \left(\frac{n_A}{1 - W_B} + \frac{2}{M_A}\right) + \left(\frac{W_B}{M_B} - \frac{n_A}{2}\right) D_B = \frac{2\gamma W_B}{RT}$$

Now, we assume that both the polymeric networks are only crosslinked with each other and there are no intra-particle crosslinks present in the system. Thus, the crosslink density of the network A is equal to that of B. Hence

$$n_A = n_B = n$$

Also, since both networks are crosslinked, the molecular weight of the network is infinite.

Hence the terms containing M_A and M_B in the denominator become zero.

$$\left(\frac{W_A}{\left(1-W_B\right)^{2/3}}\right) \times \left(\frac{n}{W_A}\right) - \frac{n}{2} = \frac{2\gamma W_B}{RTD_B}$$

Thus the simplified model is given as

$$n = \frac{2\gamma W_B}{RTD_B \left[\frac{1}{\left(1-W_B\right)^2/3} - \frac{1}{2}\right]}$$

This model was applied to the IPNs developed from modified soybean oil and polysiloxanes.
CHAPTER 3: INTERPENETRATING POLYMER NETWORKS DERIVED FROM SILYLATED SOYBEAN OIL AND POLYDIMETHYLSILOXANES

3.1. INTRODUCTION

Incorporating triglycerides into polymeric systems in an attempt to develop natural plasticizers was generally difficult due to branching and the relatively long alkyl chains of the fatty acids that resulted in incompatibility[52]. A more successful approach was to combine the triglycerides with the polymer network as an interpenetrating polymer network (IPN)[53, 54]. The broad definition of IPN is a material containing two or more components that have been vulcanized (crosslinked) in the presence of each other to form entangled (interpenetrated) networks with each other[55]. Since an IPN is inherently a multiphase system, the multiphase morphology can lead to synergistic combinations of properties that are different from the properties of the individual components or those achieved by grafting, blending or other mixing techniques. Of particular interest were the increase in toughness and fracture resistance of thermoset polymers[56]. Currently, products derived from IPN find various applications such as ion-exchange resins, adhesives, high impact plastics, vibration damping materials, high temperature alloys and medical devices[3].

Several IPNs described in previous literature contain plant oils and synthetic polymers. Some examples including alkyds and polyurethanes IPNs (also known as uralkyds) were prepared by solution casting followed by air vulcanization. These IPNs produced tough coatings that displayed high abrasion and chemical resistance[57, 58]. Similarly, IPNs of alkyds and methacrylate polymers were described[59] and the combination of soft and flexible poly(butyl methacrylate) with the hard and brittle alkyd produced a resin that had better physical properties than each of the individual components. IPNs of castor oil triglycerides with poly(ethylene terephthalate) (PET) exhibited a higher degree of toughness and faster crystallization rates than PET alone[10]. IPNs prepared from castor oil-based polyurethanes and styrene monomers could be tailoredto yield tough elastomers or reinforced plastics, depending on their compositions[11, 12].Also, IPNs based on castor oil with acrylic were elastomers and exhibited good mechanical properties[13-15]. Many other IPNs have also been prepared from functionalized vernonia oil[60], lesquerella oil, crambe oil, and linseed oil (as well as their epoxidized derivatives) with polystyrene and polyacrylics[18, 20, 22, 23, 61-63]. Most of the previous IPN work with triglycerides involved preparing a homogeneous solution of the triglycerides and the monomer, then polymerizing and crosslinking the system as phase separation occurs. Thus, the morphology of the resulting IPN was a function of the kinetics of the phase separation. In this work, we wish to report a different approach where IPNs are prepared from emulsions containing particles of silylated soybean oil and polydimethylsiloxane (PDMS).

There are numerous IPNs containing PDMS with a variety of synthetic polymers[38, 64-67] showing microphase separation and multiphase structures due to the inherent immiscibility of PDMS with most organic polymers. Many of these IPNs have interesting and useful properties because of high chain flexibility, low surface tension, high thermal stability and low Tg of the polysiloxane chain. Although there are large numbers of silicone containing IPNs, no IPNs of silicone polymers and triglyceride oils are described in literature.

Instead of using organic solvents or relying on the solubility of the monomer in the triglycerides, it is also possible to prepare oil in water emulsions of immiscible components and crosslink them before casting films. This method is known as 'Latex IPN'[68]. It consists of blending together two emulsions composed of components A and B, then crosslinking each independently with suitable crosslinkers. Alternatively, latex of polymer A is crosslinked and then monomer B, initiator and a crosslinking agent are added and polymerized[69] to yield the

desired IPN. The latter latex IPNs combine both networks in a single latex particle and as such, their morphology is limited to the size of the latex particles. The effects of the addition sequence and the polymer composition on the inter- and the intra-particle micro-domains morphology (core/shell structures) as well as the bicontinuous IPN particles structure were reviewed[70].

In this work, we focus on latex blends IPN where two emulsions of incompatible polymers are prepared separately and then combined together with a common crosslinking agent. Under these conditions, the particles from both emulsions undergo intra-particle crosslinks while still suspended in the water phase. Upon casting, additional inter-particles crosslinks take place between the coagulating particles to yield typical IPN morphology whereby the two phases are intimately mixed and crosslinked. These IPN resins that are composed of silylated soybean oil and PDMS are useful as high release liners, low friction materials or as convenient one-package protective coatings.

3.2. EMULSION POLYMERIZATION OF POLYDIMETHYLSILOXANES AND THEIR APPLICATIONS IN COATINGS

3.2.1. BACKGROUND

For coating applications, it is desirable to produce polymer emulsions from high molecular weight polymers. The high viscosity of polymers resulting from their high molecular weight makes emulsification difficult. One technique for the production of emulsions from high molecular weight polymers is to first dissolve the polymer in a solvent and emulsify the resulting solution. However, this not only involves an additional step of solvent separation into the production line increasing the cost of the product, but it also generates a high Volatile Organic Content (VOC) for the product making it undesirable for many household applications. Thus, emulsion polymerization of low molecular weight silanol terminated PDMS oligomers could be a convenient alternative to solvent-borne high molecular weight PDMS emulsions.

The technique for emulsion polymerization of PDMS is already established. It is known that factors such as solid contents or the oil phase in an emulsion, pH of the emulsion, mechanical energy dissipated for making an emulsion, and the particle size of an emulsion play important roles in determining emulsion stability. The effect of these factors on emulsion stability has been studied individually; however, the study of the collective effects and their inter-relations in order to optimize design has not previously been reported.

In this section, factors affecting emulsion stability have been explored using a statistical design of experiments. These parameters were studied individually and also the effect of these parameters on each other was demonstrated. Once the optimized design was obtained, emulsion polymerization of PDMS was carried out to generate a PDMS coating demonstrating stain resistance properties. It is known that stain resistance is a surface property and thus together with thermal and mechanical properties, surface properties like stain signal and contact angle were determined. These surface properties were then optimized based on the crosslinking density of an emulsion - by varying the factors involved in the crosslinking of an emulsion such as cure catalyst (dibutyltindilaurate, DBTDL), surfactant concentration, and the concentration of silica that was added as a crosslinking agent. An optimized design of this composition was proposed for stain resistance coating applications. Together with the analysis of surface properties, crosslinking was determined as a function of these parameters since surface, thermal, and mechanical properties of these cured films depend on the crosslinking density of the film cast. Mechanical and thermal properties of the representative films were also studied for a more complete understanding of the system.

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3.2.2. EXPERIMENTAL

3.2.2.1. Materials

Silanol terminated dimethylsiloxane oligomers of 25 cSt viscosity was purchased from Gelest Inc. (Morrisville, PA). 4-Dodecylbenzene sulfonic acid (DBSA), dibutyltindilaurate (DBTDL) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich (St. Louis, MO). Colloidal silica (NALCO-1115) containing 15 wt.% solids having particle size 4 nm was kindly supplied by Nalco Co. (Naperville, IL).

3.2.2.2. Equipment and Characterization

Thermo-gravimetric analyses (TGA, TA instruments, USA, Q500) were obtained by heating samples (approximately 8.5 mg) from room temperature (RT) to 500°C at 10°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC, TA instruments, USA, Q2000) data were obtained by first heating a sample (approximately 6 mg) under a nitrogen atmosphere to 200° C to erase any thermal history, then cooling to -70° C at 10° C/min followed by heating to 200°C at 10°C/min. The extent of crosslinking was determined by measuring the gel and swell ratios of cast films as described in the ASTM D2765-11 method [71]. The mechanical properties (stress-strain) were measured at room temperature using a Universal Testing Machine (United Calibration Corp. and United Testing Systems Inc., USA, SFM-20) according to ASTM D638 [72]. The tensile tests were performed at a strain rate of 6 cm/min and in all cases 5 specimens of each sample were tested and the average value was recorded. The molecular weight was determined by a gel permeation chromatography (GPC) equipped with a refractive index detector (Shimadzu, Japan, RID-10A) using tetrahydrofuran as mobile phase. The calibration was performed with polystyrene standards.Contact angle measurements were performed using Kruss Contact Angle Equipment (DSA100, Kruss USA, NC, USA) by placing a drop of 4 µLof water onto the film surface and measuring the contact angle over time using a static contact angle measurement method. The sessile drop method was employed to analyze the contact angle. The particle size and the particle size distribution of emulsions was analyzed using a Dynamic Light Scatterer (Zetasizer Nano S90, Malvern Instruments Inc., MA, USA) using 90 degrees scattering angle at 25°C.

3.2.2.3. Emulsion polymerization of PDMS

The preparation of high molecular weight PDMS in emulsion is well known [73, 74]. A stable emulsion was prepared by homogenizing 500 g of low molecular weight, silanol terminated dimethylsiloxane oligomers (average DP = 35), 500 g distilled water and 12.5 g DBSA in a laboratory homogenizer (Manton-Gaulin, USA, model No. 15MR) at 53 MPa. Two passes through the homogenizer under these conditions yielded a stable emulsion. This emulsion was then allowed to polymerize at room temperature and at 75°C as shown in Figure 3. 1. The rate of polymerization of these emulsions was studied by monitoring the change in molecular weight by taking periodic samples, neutralizing with 0.5N potassium hydroxide(KOH) and then precipitating the polymer in methanol. After completing the polymerization and reaching an equilibrium molecular weight, the pH of the emulsion polymer was adjusted to 10 by adding 0.5 N KOH followed by addition of silica (20 grams) and DBTDL (1.0 grams) for crosslinking. The crosslinking schematic is shown in Figure 3. 2.



Figure 3. 1 Schematic representation of polymerization of PDMS

The crosslinked emulsion (11 grams) was poured into a polystyrene petri dish with a diameter of 60 mm for film casting. These films were further analyzed for their surface and mechanical properties.



Figure 3. 2 Schematic representation of crosslinking scheme in PDMS emulsion

Following the study of the emulsion polymerization process, the process parameters were optimized by employing Box-Behnken experimental design from the statistical software Design Expert 6.0 (Stat-Ease, Inc., Minneapolis, MN). The emulsion stability, particle size and the pH of the emulsions was observed as a function of homogenizer pressure, DBSA concentration and solid content (wt. % of the oil phase) of a series of emulsions.

The optimized process of synthesis of silanol terminated PDMS emulsions was further improved by modifying the crosslinking and surface properties of the crosslinked film cast from these emulsions. Once again, the Box-Behnken statistical design was used to study the effect of concentration of crosslinking agent (colloidal silica), curing catalyst (DBTDL) and the surfactant added on the contact angle and the stain resistance of the crosslinked PDMS films.

3.2.3. RESULTS AND DISCUSSION

3.2.3.1. Emulsion polymerization of PDMS

Usually in a reversible system, high temperature and vacuum are often used to force the equilibrium toward high conversion. However, it was found that this emulsion condensation polymerization paradoxically forms a high molecular weight polymer in the presence of the water phase and proceeds to very high molecular weights under relatively mild conditions. The polymerization follows a typical suspension polymerization where monomers are polymerized in the oil droplets due to their low solubility in the water [75].

The particle size distribution during polymerization is essentially unchanged. The polymerization rate is directly proportional to temperature but the equilibrium molecular weight is inversely proportional to the temperature. Thus, it is preferred to increase the temperature for a short period of time to achieve high rates of polymerization and then cool to room temperature to achieve high molecular weight PDMS. Polymerization rates are generally higher than those reported for bulk silanol condensations in polar solvents catalyzed by strong acids [2] and are directly proportional to the surface area (e.g. particle size). A change in a number average molecular weight (Mn) and weight average molecular weight (Mw) of a typical PDMS made by an emulsion polymerization at RT is shown in Figure 3. 3.



Figure 3. 3 Emulsion polymerization of PDMS at room temperature

It is important to note that the molecular weight distribution did not increase during the polymerization (Figure 3. 4). It is well known that as equilibrium is established, low molecular weight cyclics and linear polymers are present. The relative ratio of linears to cyclics depends on the length of the alkyl side group attached to the silicon, the presence of solvent, and the type of substituents. Since these low molecular weight volatile cyclics may be a considered as a VOC, terminating the polymerization before equilibrium is achieved is a simple solution to avoid issues related to the presence of VOCs.



Figure 3. 4 Molecular weight distribution as a function of polymerization time

When high molecular weight polymers are achieved, the catalyst is neutralized with a base (e.g. KOH) and fine particle size polysilicate suspension (colloidal silica; NALCO 1115) is added. The pH is adjusted to 10 and 1% w/w DBTDL catalyst is added. At this pH, water soluble silicic acids are at equilibrium with the polysilicate particle and these water branched silicates are transported to the oil phase and are grafted onto the PDMS particles. Consequently, pre-gelled rubber particles are obtained while still in emulsion (Figure 3. 5, stage 1). It was found that the presence of these silicate grafted PDMS particles enhances the stabilization of the PDMS particles against coagulation allowing a wide variety of additives to be added at this stage [74]. Thus, films useful for coating applications can be prepared by casting anionic emulsions of silanol terminated PDMS containing alkaline dispersion of colloidal silica and DBTDL catalysts by evaporating water from emulsions.



Figure 3. 5 Schematic representation of the cure mechanisms in the water phase (stage I) and upon water evaporation and film formation (stage II) [76]

Hence, process parameters for synthesizing silanol terminated PDMS emulsions and the factors affecting emulsion stability were further investigated.

3.2.3.2. Factors affecting stability of the emulsion

3.2.3.2.1. pH of Emulsions

It is well established that emulsification of low molecular weight silicone oil (low viscosity) followed by polymerization is easier than emulsifying high molecular weight (high viscosity) oils in the absence of a solvent. Since DBSA acts as an acid catalyst as well as surfactant, the rate of polymerization of silanol terminated PDMS and the emulsion stability depends on the pH of the emulsion. Thus, a quadratic model was developed using Design Expert by employing Box-Behnken experimental design to determine the optimum pH for the emulsion.

A better fit for the model could be obtained by using a higher order equation. However, that induces local maxima or minima, which does not correspond to the trend of the data. Hence, a polynomial with lowest possible order was employed that can show a better fit. The quadratic model developed is shown below:

 $pH = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_1^2 + A_5X_2^2 + A_6X_3^2 + A_7X_1X_2 + A_8X_1X_3 + A_9X_2X_3$

where,

 $X_1 = \%$ Solids

X₂ = DBSA Concentrations [wt. %]

 $X_3 =$ Homogenizer pressure

And

 $A_0 = 9.228, A_1 = -0.159, A_2 = 0.713, A_3 = -0.0013, A_4 = 0.0007, A_5 = -0.242,$

 $A_6 = 5.768 \times 10^{-8}, A_7 = -4.333 \times 10^{-3}, A_8 = 1.446 \times 10^{-5}, A_9 = -7.000 \times 10^{-6}.$

As expected, the most significant contribution is the concentration of DBSA (A₂ and A₅).However, the decrease in the pH is not a simple linear function of the acid concentration (Table 3. 1). The fit of the experimental data to this model has the R² value as 0.6595.

Run No	Actual value	Predicted value	Residual
1	1.88	2	-0.12
2	1.67	1.55	0.12
3	1.52	1.64	-0.12
4	1.05	0.93	0.12
5	3.66	3.17	0.49
6	1.76	1.5	0.26
7	1.42	1.68	-0.26
8	1.69	2.18	-0.49
9	1.78	2.15	-0.37
10	1.32	1.7	-0.38
11	2.16	1.78	0.38
12	1.63	1.26	0.37
13	1.57	1.6	-0.034
14	1.66	1.6	0.056
15	1.55	1.6	-0.054
16	1.64	1.6	0.036
17	1.6	1.6	-0.004

Table 3.1 Experimental and predicted values of pH using a quadratic model

The goodness of fit of this model to the experimental data from the normal probability plot (Figure 3. 6) indicates that the residuals follow a normal distribution (all the experimental points follow a straight line). Thus, there is no need in this case to use any mathematical transformation to fit the response. A fairly good linear correlation was confirmed by the residual versus predicted plot (Figure 3. 7) suggesting that a quadratic model fits these data well.



Figure 3. 6 Goodness of fit for predicting pH of emulsions using a quadratic model



Figure 3.7 Predicted vs actual values obtained for the pH of emulsions using a quadratic model

The results appear to indicate a non-trivial correlation between the concentration of the acid/surfactant and pH. It is expected that the pH values will be inversely proportional to the acid concentration. Indeed, it is apparent that at low homogenizer pressure, increasing the DBSA

concentration leads to low pH. However, the PDMS phase (percent solid) also has an effect on the pH, which is increased as the PDMS content is decreased. Thus, the pH of dilute emulsions is generally higher than more concentrated emulsions. The situation is somewhat different for emulsions that were prepared under high pressure (Figure 3. 8). Under these conditions the pH is generally lower at low solid concentrations and is less sensitive on the other experimental variables.

It was observed that increasing the DBSA concentration lowers the pH of the system independently. However, the pressure and the solid content are interdependent and at higher pressure applied, the pH of the system is independent of the solids present in emulsion.



Figure 3. 8 pH of emulsions prepared at 3000 psi (A) and 8000 psi (B) as a function of DBSA and % solid

One possible explanation to this irregular dependence of pH on the concentration of the acid is the partition of DBSA between the oil phase, the surface of the emulsion particles (as a surfactant) and its solubility in the water phase. This partition depends on the size of the emulsion particles, which in turns depends on the homogenizer pressure. Thus, at lower pressure, larger particles are obtained with an overall lower surface area leading to more dissolution of

DBSA inside the water phase. Consequently, the pH will be higher in a situation where higher concentrations of DBSA are present on the interface than dissolved in the water phase.

3.2.3.2.2. Particle Size and Particle Size Distribution

Special attention was directed to study the particle size of an emulsion as a function of process parameters as it is critical for successful preparation of stable product, high molecular weight polymer and a stable process. A modified quadratic model appeared to give the best fit to the data with an $R^2 = 0.9644$ and an F-value of 9.04 which implies that this model is significant with only a 2.36% probability that the fit will be impacted by noise. A better fit for the model could be obtained by using higher order equation. However, that induces local maxima or minima, which does not correspond to the trend of the data. Hence, a polynomial with lowest possible order was employed that can show a better fit. The actual and predicted data for the particle size of the emulsions as a function of process parameters is described in Table 3. 2.

Average Particle Size = $A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_1^2 + A_5X_2^2 + A_6X_3^2 + A_7X_1X_2 + A_8X_1X_3 + A_9X_2X_3$

Where,

 $X_1 = \%$ Solids

X₂ = DBSA Concentrations [wt. %]

 $X_3 =$ Homogenizer pressure

And

$$A_0 = 22.6716, A_1 = 14.5, A_2 = -68.26, A_3 = -0.019372, A_4 = -0.1796, A_5 = -6.76, A_5 = -6.76$$

$A_6 = 1.2784 \times 10^{-6}, A_7 = 0.9333, A_8 = -1.32 \times 10^{-4}, A_9 = 0.01038.$

Run No	Actual Value	Predicted	Residual
	լուոյ	value [mm]	
1	219.7	219.7	0
2	355.8	355.8	0
3	149.1	149.1	0
4	207.5	207.5	0
5	245.8	245.8	0
6	279.6	279.6	0
7	184.3	184.3	0
8	215.9	215.9	0
9	249.2	249.2	0
10	211.2	211.2	0
11	259.8	259.8	0
12	199.7	199.7	0
13	188.5	206.36	-17.86
14	210.6	206.36	4.24
15	229.5	206.36	23.14
16	189.6	206.36	-16.76
17	213.6	206.36	7.24

 Table 3. 2 Experimental and predicted values of particle size using the chosen model

The Residuals vs. Predicted plot (Figure 3. 9) indicates an excellent linear correlation that further supports the choice of a quadratic model.



Figure 3. 9 Goodness of fit for the particle size of the PDMS emulsion using a modified quadratic model

Generally, the average particle size was inversely proportional to the homogenizer pressure and the concentration of the surfactant. The solid content also affected the particle size in a similar way where increasing the oil phase caused yielded emulsions with larger average particle size. However, the extent of each of these variables on the average particle size depends on the particular composition of the emulsion and the process itself. In order to clarify these effects the same data are presented as 3D plots.

At the lowest surfactant concentration (0.5% w/w) the average particle size increased from approximately 200 nm to 350 nm when the homogenizer pressure was set to 8000 psi (Figure 3. **10**). The average particle size also increases in a similar way at low homogenizer pressure, but the overall particle size was larger under these conditions, ranging from 250 nm to 400 nm. Surprisingly, the homogenizer pressure had very little effect on the average particle size at any solid content.



Figure 3. 10 Average particle size as a function of % solids and homogenizer pressure at low surfactant concentrations

At high surfactant concentration, lowest particles size is obtained at the highest pressure and lowest % solids (Figure 3. 11). Here again it appears that % solids impacts the particle size more than the homogenizer pressure especially under high pressure. It is apparent that the overall particle size is smaller when higher concentration of surfactant are used and the average particle size is less sensitive to changes in the pressure or the % solids.

The combined effect of the homogenizer pressure and the concentration of the surfactant can be seen from Figure 3. 12. It is apparent that at high % solids, the largest average particle size is obtained at the lowest pressure and the lowest surfactant concentration while smallest particle size is obtained at the highest pressure and the highest surfactant concentration.



Figure 3. 11 Average particle size as a function of % solids and homogenizer pressure at high

surfactant concentrations



Figure 3. 12 Average particle size as a function of homogenizer pressure and surfactant

concentration at high % solids

Closer examination clearly indicates that the effect of the surfactant concentration on the particle size is more pronounced than the homogenizer pressure at low DBSA concentration. However, the situation is reversed at high DBSA concentrations where changes in pressure are more pronounced than changes in the surfactant concentrations. As observed before, the smallest particle size is obtained at the highest pressure and the highest surfactant concentrations. Figure 3. 13 is a similar plot at low solids content. The effect of these variables is similar and the only exception is that smaller average particle sizes are obtained.



Figure 3. 13 Average particle size as a function of homogenizer pressure and surfactant concentration at low % solids

All emulsions were stable at room temperature as well as at 75°C after crosslinking with silica and DBTDL catalyst. These emulsions were used to cast films in a petri dish and different surface, mechanical and thermal properties were measured.

3.2.3.3. Analysis of film properties

Colloidal silica with an appropriate condensation catalyst (DBTDL) was added to the polydimethylsiloxane emulsion to induce crosslinking. Here, it was planned to focus on the effects of the concentration of the crosslinking silane and the amount of the crosslinking catalyst on the rate and the extent of cure. The crosslink network is obtained by condensation of water-soluble silicates with the silanol terminated PDMS. Additional crosslinks are then developed after film casting where the silanols of the polymer oil phase are condensed with the inorganic silica. The presence of silica also acts as reinforcing filler, which further increased the mechanical properties of the films.

Upon casting and evaporation of the water phase, durable films with good mechanical properties are obtained (Figure 3. 5, stage II) as interparticle siloxane crosslinks develop when silicate particles are condensed with silanol-rich PDMS at the surface of the coagulating oil particles. The crosslinking does not require any additional catalyst and no by-products (other than water) are produced. The cast films swell in "good" solvents but since they are crosslinked to a network, they retain their integrity and do not dissolve. The extent of cure can be adjusted to yield high gel fraction with essentially no free polymer chains that can diffuse and accumulate on the surface. Such diffusion of free PDMS oil is undesirable as it is known to interfere with adhesion, paintability, and in some cases can even lead to change in the mechanical properties of the films.

3.2.3.3.1. Surface properties

3.2.3.3.1.1. Contact angle θ

The determination of contact angle on the crosslinked films was an important parameter in order to investigate application of the crosslinked PDMS film for stain-resistance coatings. For the analysis of contact angle using design of experiments, a quadratic model was employed to predict the contact angle for the films. The actual fit of the experimental data to the calculated values is listed in Table 3. 3. The R² value of this model was found to be 0.9178 implying that the model appears to fit and the predicted vs. actual values of the contact angle were plotted (Figure 3. 14)

D N	Actual Value	Predicted	D (1) 1
Kun No	[nm]	Value [nm]	Residual
1	219.7	219.7	0
2	355.8	355.8	0
3	149.1	149.1	0
4	207.5	207.5	0
5	245.8	245.8	0
6	279.6	279.6	0
7	184.3	184.3	0
8	215.9	215.9	0
9	249.2	249.2	0
10	211.2	211.2	0
11	259.8	259.8	0
12	199.7	199.7	0
13	188.5	206.36	-17.86
14	210.6	206.36	4.24
15	229.5	206.36	23.14
16	189.6	206.36	-16.76
17	213.6	206.36	7.24

Table 3. 3 Experimental and predicted values of contact angle using the chosen model

It is apparent from the data (Figure 3. 15) that trend of higher contact angles was observed when the silica content was lower as the materials had progressively less surface

energy. Similar behavior was reported [77] for gel thin films containing PDMS although contact angle hysteresis rather than the contact angle itself is a better measure of water repellent property.



Figure 3. 14 Predicted vs actual values obtained for contact angle of water measured over the PDMS film surface by a quadratic model

In addition to the contact angle the surface roughness is also an important factor leading to low hysteresis, which in turn leads to a water-repellent- self-cleaning properties (lotus leaf effect). Consequently, it allows the droplet stains to remain pinned within the broader grooves. It is suggested that excess surfactant should be avoided as, in addition to these issues such as film roughness and hydrophilicity, the caracteristics of the film will be changed as it is washed away.



Figure 3. 15 Contact angle at low (A, 0.30 % w/w) and high (B, 0.9 % w/w) and concentration of sodium lauryl sulfate reactant

3.2.3.3.1.2. Staining measurements

Several stains were considered (e.g. coffee, tea, red wine, grape juice, ketchup, mustard, lipstick crayon, pen, pencil and Sharpie), however, the most troublesome staining agents – ketchup and red ink sharpie were focussed on.

The test consisted of applying drops of stain about half an inch in diameter to a clear, dry film and letting the stain set for one hour. After an hour, excess stain was gently wiped away by lightly rubbing with a wet paper towel. If the stain remained, it was then rubbed with soap and water paper towel. Initially, a numeric scale was used to evaluate the stains. However, since most of the stain was removed by the wet water towel, it was difficult to use this numeric scale as it was very subjective and is operator dependant due to optical differences between the cleaned and the original films. A free "Color Detector" program was therefore used. Thus, pictures of the fresh film and the cleaned (after the stain was rubbed) film were taken under identical light conditions and the RGB (red, green, and blue) components of the position where the stain was applied were obtained by this program. In order to further simplify the test, an average of these RGB values was taken to indicate a single numeric value. Collecting color data from the stain testing was thought to allow for a quantitative measurement of the stain. It was difficult to determine if these values agree with the rankings provided (by Sherwin-Williams) due to the fact that most of the stains were removed and there were only minor changes in the appearance of the films. It should be mentioned that this test procedure is similar to ASTM D7514-09.

3.2.3.3.1.2.1. Ketchup Stains

Due to the minute differences in the staining it was difficult to find a good model, the best fit was obtained using quadratic model with the R^2 value to be 0.6359. The poor fit (Table 3. 4) is demonstrated in the goodness of fit plot that shows the low correlation between the predicted and actual values (Figure 3. 16).

 Table 3. 4 Experimental and predicted values of ketchup stains (average of RGB values obtained) using the chosen model

Run No	Actual Value	Predicted value	Residual
1.00	164.67	164.29	0.38
2.00	166.17	160.67	5.50
3.00	160.83	166.33	-5.50
4.00	164.83	165.21	-0.38
5.00	169.00	171.15	-2.15
6.00	168.50	175.77	-7.27
7.00	178.83	171.56	7.27
8.00	164.33	162.19	2.14
9.00	164.00	162.23	1.77
10.00	189.00	181.35	7.65
11.00	163.83	171.48	-7.65
12.00	157.17	158.94	-1.77
13.00	161.17	163.28	-2.11

Due to an only fair goodness of fit, the data are best viewed qualitatively with an emphasis on the trends instead of the actual values. Thus, at low surfactant concentration, it is observed that the silica content has little or no effect on staining and only the tin catalyst is the major factor. Apparently, at low catalyst concentrations much of the silicate is not reacted with the oil phase, which leads to a more hydrophilic surface and poorer stain resistance.



Figure 3. 16 Predicted vs actual values for ketchup staining using a quadratic model

The situation was somewhat different when high concentration of the surfactant was used. In this case excess of surfactant appeared to accumulate on the surface of the film when the water evaporated. Although no stain was observed, the nature of the surface changed and this is reflected in the different RGB values. It is noticeable from Figure 3. 17 that these changes are very small and the surfactant has only a minor effect on the stain resistance. Further, any excess will be washed away upon rubbing.



Figure 3. 17 Effect of silica content and concentration of tin catalyst (DBTDL) on staining for low (A) and high (B) surfactant concentration

3.2.3.3.1.2.2. Red Ink Sharpie Stains

The staining results with this stain were very similar to the previous results obtained with the ketchup. In both cases the most important variable was the degree of cure of the film. Thus, incomplete cure and high concentrations of "free" water soluble silicates lead to rough and hydrophilic surface over the smooth hydrophobic PDMS surface, which results in poorer stain resistance. Due to these results showing that all the films were similar in stain resistance, it was not possible to further optimize the formulation.

Two samples are shown below (Figure 3. 18 and Figure 3. 19) which clearly show the stains are easily washed away from the surface.



Figure 3. 18 Ketchup stained film (left) prepared with 5.0 % wt Nalco 1115 silica and 0.25 wt %





Figure 3. 19 Red sharpie stained film (left) prepared with 5.0 % wt Nalco 1115 silica and 0.25

wt % DBTDL and same film lightly rubbed with wet towel (right)

3.2.3.3.2. Crosslinking Density

The degree of swell and the gel fraction were measured as a function of silica content in the PDMS films for two different cure catalysts concentrations. The equilibrium swell ratio (Q) was calculated using equation 1:

$$Q = \frac{W_{P0} / d_P + W_s / d_s}{W_{P0} / d_P} \quad (1)$$

where, W_{P0} is the initial weight of the sample, W_S is the weight of the solvent in theswollen sample at equilibrium, d_P the density of the sample and d_S is the density of the solvent.

The gel fraction (G) was calculated using equation 2:

$$G = \frac{W_P}{W_{P0}} \times 100 \quad (2)$$

where, W_P is the weight of the dried sample after all the extractable sol was removed while swelling.

The swell ratio of various films prepared with different amounts of Nalco1115 is shown in Figure 3. 20. The data are dispersed but it is appears that the swell ratio is inversely proportional to the silica concentration. Thus, higher concentrations of silica lead to higher concentrations of soluble silicates which were the crosslink agents in the system resulting in higher crosslink density. It can also be seen that higher swell ratios were obtained for lower concentrations of cure catalyst (DBTDL) indicating lower crosslinking. However, for higher silica content, their swell ratios are almost the same indicating that the films were completely crosslinked and swelling became independent of silica or DBTDL concentrations.



Figure 3. 20 Swell ratio of cast films in toluene

The gel fraction of the same films is shown in Figure 3. 21. The data indicates that the gel fraction increases slightly as a function of silica content. Also, the gel fraction is higher for the higher DBTDL content indicating the higher crosslinking present whereas, the gel fraction for the lower DBTDL content is lower and almost independent of the concentration of silica.



Figure 3. 21 Gel fraction of films after swelling and drying from toluene

Similar data were also obtained with different types of silicas. However, films with the best mechanical properties were obtained wih Nalco 1115 colloidal silica.

3.2.3.3.3. Mechanical Properties

It is essential to leave the formulated emulsion for at least 4 days at RT at the pH of 10 in order to ensure sufficient soluble silicate is obtained to intiate crosslinks and network development. Under these conditions the cast films are cured and appear as elastomeric films.



Figure 3. 22 A typical stress-strain curve for the crosslinked PDMS films

A typical stress-strain curve is shown in Figure 3. 22. This film was obtained from an emulsion which was formulated with 5 wt% Nalco 1115 and 0.25 wt% DBTDL after aging the emulsion at RT. These elastomers are characterized by relatively low initial modulus and very high elongation in the range of 600-800%. The tensile strength is typical to silicone rubber and is in the range of 120-160 psi. Since the silica acts as a reinforcing filler in the system, the ultimate mechanical properties are directly related to the concentration of silica.

3.2.3.3.4. Thermal Properties

The thermal properties of cast films from the silicone emulsions were studied by DSC (Figure 3. 23) and TGA (Figure 3. 24). Typically, the emulsions were allowed to cure for at least 4 days to ensure complete crosslinking. For the DSC sample was heated to 200°C at 10°C/min held at this temperature for 5 minutes to erase the thermal history, then, cooled at 10°C/min to - 70°C, held at this temperature for 5 minutes and finally heated at 10°C/min to 200°C. The results show a crystallization peak at -67.8°C and a melting peak at -43.4°C films with no other transition over this wide temperature range is well known for PDMS.



Figure 3. 23 Typical DSC plot of crosslinked film of silicone emulsion

TGA was run at 20°C/min from RT to 450°C (Figure 3.24). A very small (~2 wt.%) weight loss was observed below 200°C most likely due to residual water in the sample followed by thermal degradation above 300°C. This relatively low degradation temperature compared with typical PDMS is due to the presence of KOH in the sample that was added to neutralize DBSA which acts as a de-polymerization catalyst at elevated temperatures.



Figure 3. 24 Typical TGA of the crosslinked film cast from silicon emulsion

3.2.4. CONCLUSIONS

The overall objective of this work was to prepare and characterize single-package, crosslinked PDMS coatings from emulsions of silanol terminated PDMS and colloidal silica. Throughout this work, a Box-Behnken statistical design experiment approach was used to optimize selected key properties. In this project, a statistical design of experiments was developed in order to determine optimum conditions and properties with respect to the key parameters involved. These parameters affect the process in terms of the total process time, process cost and the reproducibility of the process. Thus, the optimum conditions developed in this project are scalable and can be used for commercially scalable product.

The silicone emulsions made typically have 30% or more solids and emulsions with up to 60% solids were made. Since they are water- based emulsions; they do not contain any solvent and could be considered as "no-VOC" emulsions. Another important property of these emulsions

is that they can be formulated with different pigments, fillers or viscosity modifiers for a specific application without disturbing the emulsion stability.

The major advantage of this technology is that crosslinking can be introduced in an emulsion without breaking the emulsion. The crosslinking density can be varied depending on the types and quantities of silica content and crosslinking agent added. However, these emulsions, upon casting films for coating applications, can be cured at ambient conditions and without any additional parameters such as higher temperature or UV exposure. Upon curing, the coatings show good adhesion to various substrates like glass, wood, brick etc. suggesting applicability as good coating materials. These experiments were performed empirically without applying the standard procedure for these substrates. The in-depth analysis on the adhesion was performed by our industrial partners and the data is confidential.

3.3. SYNTHESIS AND SYNTHESIS AND CHARACTERIZATION OF SILYLATED SOYBEAN OIL FOR ITS APPLICATION IN IPNS

3.4.1. BACKGROUND

The most widely used method for the synthesis of organosilicones is hydrosilylation. It involves insertion of Si-H to alkenes using platinum or transition metal catalysts or a free radical catalyst [78-80]. The method is particularly effective with terminal unsaturation. Internal double bonds can only be hydrosilylated using chlorosilanes, however, chlorosilanes are extremely corrosive and flammable.

Another approach to the synthesis of organosilicones is carbosilylation. This method does not generate new Si-C linkages, it is more efficient than hydrosilylation, and the reaction does not create any by-products. [81-84]. The reaction is efficient for terminal unsaturation with allylsilanes, but more effective than hydrosilylation when targeting internal double bonds. The major disadvantage of carbosilylation when compared with hydrosilylation is that carbosilylation is limited to allylsilanes and cannot be used with vinylsilanes.

Another approach to functionalize alkenes with vinylsilanes is "trans-silylation" by using transition-metal-catalyzed silylative coupling. The mechanism of this reaction involves the insertion of vinylsilane into the metal-hydrogen bond to generate the metal-silicon species followed by insertion of the alkene with elimination of the substituted vinylsilane[85-87]. From a recent comprehensive review [88] it can be concluded that the mechanism of silylation of alkenes by trans-silylation is similar to that of hydrosilylation. Thus, this method is more appropriate for silylation of alkenes containing terminal unsaturation than for alkene having internal double bonds.

The preferred approach to silylate 'internal' double bonds is to employ the 'Ene' reaction which is a subset of the well-known Diels-Alder reaction [89]. The first example of a Lewis-acid promoted carbonyl–Ene reaction using vinylsilane as the ene moiety was published in 1990 [90] and most of the explored 'Ene' reactions have involved addition of vinylsilanes to carbonyl groups. A recent comprehensive review of 'Ene' and Diels–Alder reactions involving vinyl and allylsilanes with emphasis on silyl-substituted 1,3-butadienes building blocks in organic synthesis is available [91]. Generally, the allylic system reacts similarly to a diene in a Diels-Alder reaction and unless catalyzed, requires high temperatures due to the high activation energy requirement needed to cleave the allylic C-H σ -bond. It is important to note that the addition of vinyl silane to olefins via the 'Ene' reaction does not depend on the position of the double bond in the olefin and was found to proceed to high yields even with non-terminal double bonds.
The objectives of this work were to silylate soybean oil by grafting trimethoxyvinylsilane onto the unsaturated fatty acid triglycerides to introduce crosslinkable functional groups into the soybean oil backbone. This strategy is based on a process that is relatively simple and free of any hazardous compounds; eliminating all potentially toxic or expensive metal-based catalysts that were traditionally used for silylation of organic compounds.

In this section, the silylation of soybean oil based on previous publications was studied [47, 92-94]. The objective was to optimize the process with respect to the reaction parameters such as reaction time, reaction temperature, and the composition of the reaction mixture. The process was also studied and optimized in order to reduce side-reactions involving redistribution reactions of methoxysilanes with triglycerides. Once the process was optimized, the product was further investigated for its crosslinking properties such as the rate of cure based on the cure conditions. The optimized silylated soybean oil was used further for making several interpenetrated polymer networks with polysiloxanes for various coating applications.

3.4.2. EXPERIMENTAL

3.4.2.1. Materials

LowSat® soybean oil was kindly provided by Zeeland Farm Services, Inc. (MI, USA). The vinyltrimethoxysilane (VTMS) was purchased from Gelest, Inc. (PA, USA). The catalyst Luperox-101, and triethylamine (TEA) were purchased from Sigma-Aldrich (MO, USA). All chemicals were reagent grade and were used without further purification unless noted.

3.4.2.2. Silylation procedure

In a typical reaction LowSat[®] soybean oil, VTMS and Luperox-101 catalyst (1 wt. %) were mixed and added to a 2L PARR reactor (PARR Instrument Company, IL. USA, PARR

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4841). The reactor was purged with nitrogen and the reaction mixture was heated to the desired temperature for a predetermined period of time under constant stirring to graft VTMS onto the soybean oil via the Ene reaction [95] as described in Figure 3. 25. The grafting of VTMS onto the soybean oil was confirmed by ¹H NMR. The effect of temperature ($225^{\circ}C - 275^{\circ}C$), Time (1 hour – 13 hours) and the initial composition of soybean oil to vinyltrimethoxysilane (1:1 – 1:2) on the grating of the VTMS to the soybean oil was studied using a statistical design of experiments. A Box – Behnken statistical design was used in the software Design Expert 6.0 (Stat-Ease, Inc., Minneapolis, MN) to understand and optimize the process.



Figure 3. 25 Silylation of unsaturated fatty acids in soy oil triglycerides with VTMS by the "Ene reaction"

Once the silvlation was complete, the curing of typical silvlated soybean oil (SilSoy) was studied using a statistical design of experiments with the Box- Behnken design. The curing mechanism of the silvlated soybean oil was monitored by methanol evaporation as described in Figure 3. 26. The crosslinking was studied as a function of cure-temperature, water content and the amount of condensation catalyst (TEA) and the methanol evaporation was monitored by isothermal TGA.



Figure 3. 26 Hydrolysis and condensation of alkoxysilanes grafted onto the soybean oil molecule

3.4.2.3. Characterization

Thermogravimetric analyzer (TGA, TA instruments, USA, Q50) was used to determine the extent of grafting of the VTMS onto the unsaturated fatty acid in the triglyceride oils. The weight loss of a sample was recorded by heating the sample isothermally at 130°C (above the boiling point of the VTMS) for 20 minutes to completely remove any unreacted silane. The extent of grafting was then calculated based on the weight loss of the sample related to the free (not grafted) VTMS.

The structure of the silylated products was determined by ¹H NMR with 500 MHz NMR spectrometer using a solvent peak as an internal standard (Varian Inc., USA, Varian Unity Plus). The viscosity was measured using a Brookfield digital viscometer (Brookfield Engineering, USA, LVDV-E) equipped with spindle LV-1 (61) suitable for a viscosity range of 15 - 20,000 cPs.

3.4.3. RESULTS AND DISCUSSION

3.4.3.1. Characterization of the silylated low-sat soybean oil

LowSat[®] soybean oil was chosen for the grafting reaction since the lower saturated content ensures that a coating prepared from it will contain few unreacted triglycerides. This soybean oil has an average of 5.1 carbon-carbon double bonds per triglyceride compared with 'regular' soybean oil that contains an average of 4.5 carbon-carbon double bonds per triglyceride. The higher unsaturated content (and the lower concentration of saturated fatty acids) provides for higher probability that no triglyceride molecule will contain only unsaturated fatty acids as this will lead to incomplete cure and poor coating.



Figure 3. 27 Partial ¹H NMR spectrum of soy oil (a), intermediate reaction with VTMS (b), and the final silylated soy oil product

A high degree of grafting of VTMS onto the soybean oil was achieved by the 'Ene reaction' as observed by ¹H NMR (Figure 3. 27). The chemical shift of the protons associated with the double bonds of the fatty acids in the soybean oil appears around 5.25 ppm (Figure 3.

27A). The partial ¹H NMR spectrum of an intermediate product from the reaction of soybean oil with VTMS is shown in Figure 3. 27B. It is apparent that the protons of the double bond in the VTMS appear as a multiple resonance peaks near 6.0 ppm. Furthermore, the complex shape of the resonance peaks related to the unsaturation of the soy oil also changed as the reaction proceeded. The final silylated product is shown in Figure 3. 27C, which clearly indicates the disappearance of the resonance peak, associated with the unsaturation of the VTMS near 6.0 ppm. It should be emphasized that unlike hydrosilylation reactions, the 'Ene reaction' mechanism consumes the unsaturation linkages in VTMS but the end product still contains unsaturation. The yield of this grafting can be calculated from the initial mass ratios of the reactants and was found to be 95%.





The extent of grafting by a typical silvlation reaction was confirmed by isothermal TGA experiments conducted at 130°C. This temperature was chosen since it is above the boiling point of VTMS (123°C) but well below the degradation temperature of soy oil. Under these conditions all free (not grafted) VTMS will be removed and the yield of the grafting reaction can be

determined from the weight loss. Indeed, it is apparent from Figure 3. 28 that all the unreacted VTMS was removed within 15 minutes, indicating the unreacted fraction to be 6 wt% of the total mass of the sample. The extent of grafting was calculated using Equation 3 by extrapolating the observed weight loss knowing the initial composition of the sample.

$$\%Grafting = \frac{(\% VTMS \text{ in feed}) - (\% VTMS \text{ loss})}{\% VTMS \text{ in feed}} \times 100 \qquad (3)$$

3.4.3.2. Effect of reaction conditions

The effect of reaction temperature, time and the molar ratio of soybean oil to VTMS on the extent of the grafting reaction of VTMS on the LowSat[®] soybean oil could be demonstrated by a quadratic model with the best fit. The R^2 value for the model is 0.9226. The plot of actual grafting values obtained with that of predicted values (Figure 3. 29) shows that the model is a proper fit for the experimental data.



Figure 3. 29 Predicted versus actual values for grafting demonstrated by a quadratic model

It was found that at constant reaction temperature, the degree of VTMS grafting on soybean oil backbone increases rapidly as a function of reaction time (Figure 3. 30). The apparent increase in grafting is not significant with respect to the molar ratio of the reactants. The maximum grafting of VTMS was obtained for the highest reaction time and the lowest molar ratios of soybean oil to VTMS. Similarly, the grafting was found to be highly dependent on the reaction temperature as compared to the molar ratios of the reactants (Figure 3. 31). It is apparent from the figure that for a constant reaction time, the degree of grafting is almost constant for the range of molar ratios observed, but it is directly related to the reaction temperature. Hence, it can established that the extent of grafting of VTMS on the soybean oil backbone is directly proportional to the reaction time and the temperature of the reaction. However, the molar ratios of the reactants does not affect the grafting of the reaction significantly.





constant temperature



Figure 3. 31 Degree of grafting as a function of reaction temperature and the ratio of the reactants at constant reaction time

It should be noted that when the reaction was allowed to run at high temperatures for a long period of time a siloxy-ester exchange reaction was observed. Under these conditions, the methoxy groups of VTMS can react with an ester group of the triglyceride (Figure 3. 32) to form new Si-O-C linkages. The formation of methyl esters via this reaction explains the relatively small but apparent weight loss in the TGA spectrum (Figure 3. 28) in contrast to essentially no weight loss of the soy oil under identical heating conditions. These redistribution reactions about a silicon atom are well known and were reviewed previously [96]. The redistribution depends on the nature of the ligands. It was reported that the redistributions of alkoxy ligands in the absence of a catalyst is generally less facile and slow at temperatures of 150°-200°C but quite rapid in the presence of catalysts [97].



Figure 3. 32 Redistribution side reaction between VTMS and the carbonyl group of the triglyceride

This redistribution reaction was also studied as a function of silylation reaction conditions – temperature, time and composition of reactants. The slope of the tangent line drawn to the weight loss curve of TGA at 130°C at the end of 20 minutes is modelled with a quadratic model with theR² value to be 0.8373. A fairly good correlation was observed for the plot of predicted versus actual values. Figure 3. 33shows that the model fits the actual data well.



Figure 3. 33 Predicted versus actual values for redistribution reaction as demonstrated by a quadratic model

At higher temperature (275°C), the TGA slope was found to decrease rapidly as a function of reaction time but it was independent of the molar ratios of the reactants (Figure 3. 34).



Figure 3. 34 TGA slope as a function of reaction time and the ratio of the reactants at constant reaction temperature

Thus, it could be concluded the higher reaction time is favorable for the redistribution reaction. This observation is also supported by Figure 3. 35. As discussed before, the redistribution reaction is highly dependent of the reaction temperature and the redistribution of alkoxy ligands is active only at higher temperatures (Figure 3. 35).



Figure 3. 35 TGA slope as a function of reaction temperature and the ratio of the reactants at

constant reaction time

At constant molar ratio (2:1) of soybean oil with VTMS, the redistribution reaction was found to be directly related to the reaction temperature and the reaction time. The slope of the TGA decreases (Figure 3. 36) and attains the minimum point (extent of the redistribution reaction is the highest) at highest temperature (275°C) and time (13 hours).





It is interesting to note that unlike redistribution reactions about the silicon atom, the observed redistribution reaction here involves a silyl-ester exchange reaction. Furthermore, this redistribution reaction occurred in the absence of water (no hydrolysis) or a catalyst and proceeded, although slowly, by simple heating.

Throughout the experiment, it was found that the degree of grafting as well as the side reaction during silulation of soybean oil with VTMS is nearly independent of the molar ratios but highly dependent on the reaction temperature and time. It is therefore recommended that similar grafting reactions onto organic esters by the 'Ene' reaction should be conducted at low temperatures. However, if elevated temperatures are used, short reaction times are preferred in order to maximize the yield and minimize the extent of the redistribution reaction.

Also, although it is possible to remove the unreacted fraction of VTMS by distillation, it was deemed unnecessary since upon hydrolysis and condensation to yield IPNs all the siloxy groups, whether grafted or free, will be part of the network.

3.4.3.3. Moisture cure

Silicone moisture activated cure systems are well known and are based on the hydrolytically unstable Si-O-C linkages. Thus, upon exposing oils containing alkoxysilanes to atmospheric water hydrolysis to silanols and subsequent condensation to stable siloxane bonds (Si-O-Si linkages) occurs and this leads to crosslinked films as shown schematically in Figure 3. 26. It is important to note that this cure occurs at room temperature and does not require pre-mixing (e.g. it is a one-componentsystem) or a diluent.

The crosslinking reaction was monitored by methanol evaporation as a result of the hydrolysis of alkoxysilanes grafted onto the soybean oil molecule. The conventional methods of determining the curing by change in the viscosity could not be used for the system due to the viscosity gradient formed between the exposed surface and the unexposed surface of the silylated soybean oil at the given conditions. A modified quadratic equation was predicted for the methanol evaporation as a function of cure temperature, water content and catalyst concentration. A straight line passing through the origin shows that the actual data fits well with the predicted data for methanol evaporation (Figure 3. 37).





At constant catalyst concentration, the cure rate was observed to be dependent on both the water content and the curing temperature of the silylated soy (Figure 3. 38).



Figure 3. 38 Cure rate as a function of water content and the cure temperature at constant

catalyst concentration

This is because higher water content ensured the hydrolysis of more alkoxysilane groups to silanols, thus producing more methanol in the system. Due to the higher temperature of curing, the methanol evaporates rapidly and the reverse reaction of the methanol to alkoxysilanes is prevented. At constant water content, however, the curing is highly dependent on the cure temperature (Figure 3. 39) and catalyst concentration does not play a significant role in the rate of curing.

This is because a very small amount of catalyst is sufficient for the condensation of silanols to siloxanes to form gel. The process of silanol condensation is a rapid process while the hydrolysis of alkoxysilanes is a rate limiting step [98]. Thus, at higher temperature, the removal of methanol formed by hydrolysis is faster thus preventing back-condensation and driving the forward reaction.





constant water content

Hence the temperature of curing and the water content in SilSoy have synergistic effects on the rate of curing as monitored by methanol evolution. Figure 3. 40 demonstrates the effect of cure temperature and water content on methanol evolution derived from the quadratic model. This agrees with the results obtained in Figure 3. 38 and Figure 3. 39 completely.





3.4.4. CONCLUSIONS

Vinyltrimethoxysilanes were grafted onto unsaturated fatty acids of various natural oil triglycerides by the 'Ene' reaction. The chemical structure of the silylated oils was analyzed by ¹H NMR and the extent of grafting was calculated by TGA. The silylation reaction was studied using a statistical design of experiments and it was found that the grafting of silane onto the soybean oil molecule is a function of reaction time and reaction temperature. However, under extreme temperatures and long reaction times, a siloxy-ester exchange reaction was identified whereby an alkoxy group of the silane can undergo a redistribution reaction with a methoxy

group from the fatty ester. This redistribution reaction was also studied using statistical design of experiments and optimal reaction conditions were determined to reduce this reaction. The low viscosity silylated oils thus obtained can be used as a moisture curable coatings and the cure kinetics of the typical silylated soybean oil was studied as a function of curing conditions. The curing was observed to be highly dependent on water content and curing temperature. The cured silylated soybean oil could be used for variety of coating applications including general protective coatings on a variety of substrates including biobased paper coatings.

3.5. INTERPENETRATING POLYMER NETWORKS DERIVED FROM SILYLATED SOYBEAN OIL AND POLYDIMETHYLSILOXANES

3.4.1 BACKGROUND

Interpenetrating Polymer Networks were prepared from emulsions of silylated soybean oil (SilSoy) and polydimethylsiloxane (PDMS). The optimization of emulsion polymerization of PDMS has been discussed in Section 1 and the process of synthesis of SilSoy has been discussed in Section 2. These materials were used for the synthesis of IPNs and are discussed in this section.

3.5.1. EXPERIMENTAL

3.5.1.1. Materials

Low-saturated soybean oil was kindly supplied by Zeeland Farm Services (Zeeland, MI). Silanol terminated dimethylsiloxane oligomers of 25 cSt viscosity and vinyl trimethoxysilane (VTMS) were purchased from Gelest Inc. (Morrisville, PA). 4-Dodecylbenzene sulfonic acid (DBSA), dibutyltindilaurate (DBTDL), sodium dodecyl sulfate (SDS) and 2,5-Bis (tertbutylperoxy)-2,5-dimethylhexane (Luperox[®]101) peroxide, were purchased from Sigma-Aldrich (St. Louis, MO). Colloidal Silica (NALCO-1115) 15 wt.% solids having particle size 4 nm was kindly supplied by Nalco Co. (Naperville, IL).

3.5.1.2. Equipment and Characterization

The equipment used for the synthesis and the analysis of the IPNs have been described in the section 1 and section 2 of the chapter 3. The equipment not used before is described in this section.

The mechanical properties (stress-strain) were measured at room temperature using a Universal Testing Machine (United Calibration Corp. and United Testing Systems Inc., USA, SFM-20) according to ASTM D638[72]. The tensile tests were performed at a strain rate of 6 cm/min and in all cases at least 5 specimens of each sample were tested and the average value was recorded.

Scanning electron microscope (SEM, Japan Electron Optics Laboratories, Japan, JEOL-6400V) was used to study the morphology of fractured surfaces. A fresh surface was obtained by fracturing the specimen in liquid nitrogen. The fractured surface was fixed with 1% Osmium Tetroxide (OsO4) solution to stain the unsaturation of the soybean oil. Each image was observed under backscatter electrons detector for better resolution and contrast. Thus, the silylated soybean oil appears as a lighter shade while the polysiloxane appears as a darker shade.

3.5.1.3. Silylated soybean oil emulsion

The silulation of soybean oil was performed by grafting VTMS onto the soybean oil by the Ene reaction[95] as shown in Figure 3. 25. The detailed description of the process was given in the section 3.2 of this chapter.

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The silvlated soybean oil (900 g) was homogenized with SDS (22.5 g) in a laboratory homogenizer (Manton-Gaulin, USA, model No. 15MR) at 53 MPa to yield 45% solids in the emulsion. Two passes through the homogenizer under these conditions yielded a stable emulsion. Upon aging, the hydrolytically unstable methoxysilanes hydrolyzed to form silanol functional groups attached to the soybean oil.

3.5.1.4. Emulsion polymerization of polydimethylsiloxane

The emulsion polymerization of PDMS has been described in section 3.1 in detail. The PDMS emulsion made by the procedure described was synthesized and then incorporated into the IPN system.

3.5.1.5. Preparation of soybean oil-PDMS IPNs by the emulsion method

Various IPN compositions were prepared simply by mixing different amounts of the PDMS and the silylated soybean oil emulsions, then casting films and allowing the water to evaporate at RT. In all cases, the mixed emulsions were stable with no apparent coagulation or creaming. Similarly, no apparent gross phase separation was observed in the cast films after the water was evaporated.

3.5.1.6. Calculation of Biobased Content of the Latex IPNs

The biobased content of the IPNs was calculated based on the calculations mentioned in the literature [99].

The total biobased content for the multi-component system was calculated using the following equation:

$$BCC_{prod.} = \frac{\sum (W_n \times BCC_n \times OCC_n)}{\sum (W_n \times OCC_n)}$$

Where,

BCCn = Biobased Carbon Content of the nth component.

OCCn = Organic Carbon Content of the nth component.

Wn = Mass of the nth component.

3.5.2. RESULTS AND DISCUSSION

3.5.2.1. Formation of IPN

Network formation is obtained in two stages via siloxane crosslinks: in the first stage, silicates that were introduced via partial dissolution of colloidal silica in the alkaline pH of the mixed emulsion lead to crosslinked silicone particles. As described previously[100] these soluble silicate species are grafted onto the silanol chain-ends of both PDMS and the silylated soybean oil. This silanol condensation reaction is catalyzed by DBTDL leading to intra-particle crosslinks. In the second stage, additional inter-particle crosslinks are obtained upon evaporation of the water phase between the coagulating emulsion particles. These inter-particle crosslinks, through additional silanol-silanol condensations, further contribute to the overall network via condensation reactions between the terminal PDMS silanols, silanol grafted soybean oil and the inorganic silicates/silica filler. The small silica particles further act as a reinforcing agent to reinforce the entangled crosslinked network as shown schematically in Figure 3. 41.

It should be noted that since all the components in this system contain terminal silanols, their condensation to yield stable siloxanes linkages is the basis for the crosslinks of the network. These crosslink linkages connect all components to the network and include siloxanes linkages between the triglycerides, PDMS and silica. Siloxane linkages between adjacent fatty acids of the same triglyceride or the formation of macrocyclic PDMS cannot be ruled out. These siloxanes linkages are considered as defects and will not contribute to the network. However, due to the large number of silanols the number of such defects is expected to be negligible. Furthermore, as depicted in Figure 3. 41, it is expected that not all silanols will be condensed to siloxanes and will remain as Si-OH. This residual silanols and silicates are advantageous as they act as adhesion promoters and enhance the adhesion of these IPNs to inorganic substrates such as glass, cement, concrete, brick, aluminum and steel.



Figure 3. 41 Schematic representation of IPNs composed of siloxane cross-links between high MW PDMS, silylated soy oil, and silica filler particles

3.5.2.2. Morphology

The morphology of the IPNs is greatly affected by the relative concentrations of PDMS and silvlated soybean oil as observed in the SEM micrographs (Figure 3. 42 A-D). All four micrographs indicate distinct phase separation that changes with the ratio of the silvlated soybean oil (component 1) and PDMS (component 2). For better distinction between these two components the IPN samples were stained with OsO4 prior to their examination in the SEM and the images were captured using a backscattering mode. Since OsO_4 adsorbs onto the double bonds, it stains only the silylated soybean oil phase containing the unsaturated fatty acids and, hence, this component appears as the bright phase in the backscattering mode. As the concentration of one component is increased and the other is decreased, a dual phase morphology is observed followed by a bicontinuous morphology and then again a dual phase morphology. Thus, the IPN containing 20wt% silylated soybean oil (Figure 3. 42A) shows the PDMS-rich phase (component 2) as the continuous matrix with the silylated soybean oil phase (component 1) dispersed in it as fine globular nodules, about 5-15 μ m in size. Further increasing the concentration of the silylated soybean oil to 40 or 60 wt.% (such that it is present at about the same concentration as PDMS) leads to a co-continuous morphology (Figure 3. 42B and Figure 3. 42C). The globular nature of the domains is still visible but the continuous phase is less distinct giving rise to the appearance where all the globular domains are stuck to each other.



Figure 3. 42 SEM images of IPNs composed of different concentrations of silylated soybean oil/PDMS. (a) 20/80, (b) 40/60, (c) 60/40, and (d) 80/20

Upon further increasing the concentration of the silylated soybean oil to 80 wt.% (Figure 3. 42D) leads again to dual phase morphology. However, here the continuous phase is the silylated soybean oil matrix and the dispersed phase consists of globular PDMS domains about 0.5-2 µm. Similar changes in the dual phase morphology were noted before when component 1 of an IPN was dispersed in component 2 at low concentrations and appeared as the dispersed phase. However, upon increasing the concentration of component 1, it then became the continuous phase and component 2 became the dispersed phase [55].

The presence of phase separation and globular domains structure are influenced primarily by the extent of the miscibility between the silylated soybean oil matrix and PDMS. However, in this case the shape of the domains is also determined by the intra-molecular crosslinks that were induced in the emulsion phase in both particles. These crosslinks in each phase prevent unrestricted flow upon coagulation and film formation and restrict the shape of the domains. Since the crosslink density of each component need not be the same, it is expected that these variations in the morphology will have significant effects on the mechanical properties.

It is also important to note that no cracks, voids or other defects are observed along the interface between the globular domains and the matrix. Thus, the intimate interface between the soy phase and the PDMS phase is expected to minimize any macro phase separation.

3.5.2.3. Gel-Swell analysis

The degree of swell and the gel fraction were measured as a function of composition of the IPNs (Figure 3. 43). The equilibrium swell ratio (Q) was calculated using Equation 1 and the gel fraction (G) was calculated using Equation 2 mentioned in the section 3.1.

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The degree of swell is related to the free chain length between crosslinks and to the interaction of the solvent with the polymer chains. Thus, low crosslink density leads to high degree of swell and usually low gel fraction. However, it is apparent that the crosslinked hompolymer PDMS gel exhibited relatively high swell and high gel fraction while the sample containing crosslinked silylated soybean oil exhibited low gel fraction and relatively low swelling (Figure 3. 43). This combination is highly unusual and not commonly observed in polymeric systems. One possible explanation could be related to a variation in the interactions of the solvent with each component of the IPN.



Figure 3. 43 Gel and swell fractions of IPNs composed of different concentrations of silylated soybean oil/PDMS

In the extreme case, the toluene solvent is a 'good' solvent for PDMS but a poor solvent for the soy component. Under this condition the soy oil component will not swell and will show high gel fraction even if it is not crosslinked. However, this is not the case here since toluene is a 'good' solvent for both the PDMS and the soy components. Apparently, the network in these IPNs is non-uniform and the silvlated soybean oil phase contains a high density of localized crosslinks (e.g. tight network), leading to low swelling of these regions. However, other regions contain no crosslinks and therefore do not contribute to the gel content. Thus, the data indicate that only about 30 wt.% of the silvlated soybean oil sample is crosslinked (70 wt.% is soluble in toluene), but these crosslinked regions contain a relatively high density of crosslinks leading to a low swell ratio of these regions. In comparison, the cured PDMS sample (containing no silvlated soybean oil) exhibits a fairly high degree of swelling and also a high gel fraction. Thus, the network in this sample is more uniform and complete, leading to high gel content but the overall crosslink density is low resulting in a high degree of swelling.

A model was developed in chapter 2 based on the Donatelli's equation to predict the crosslink density of IPNs (equation 3). The main variables in this derivation are the average diameter of the dispersed phase, the composition of polymers and the interfacial energy between the two polymer phases. Since the two polymers are inherently incompatible, some micro-phase separation occurs even when the polymers are intimately mixed as depicted in Figure 3. 42.

$$n = \frac{2\gamma W_B}{RTD_B \left[\frac{1}{\left(1 - W_B\right)^2 / 3} - \frac{1}{2}\right]} \quad \dots \dots \dots \dots (4)$$

where, n_A : crosslinking density in moles/cm³

 W_B : weight fraction of the dispersed phase

R: Gas constant in J/mole

T: Temperature in K

 D_B : The domain diameter of the dispersed phase in nm

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 γ : Interfacial energy between the two phases in dynes/cm

Since the crosslinking reaction in both components is identical and is based on the formation of siloxanes linkages by silanol condensation, the gel and swell fractions of each IPN are observed to be between these two extremes and depend on the composition of the sample. In general, it is observed that the gel content and the swell ratio are inversely proportional to the concentration of the silylated soybean oil content. Conversely, increasing the concentration of PDMS in the IPN leads to a more uniform crosslink structure and a higher gel fraction. However, due to the relatively low degree of crosslinking it also leads to a higher swell ratio.

Although, it was realized that the compositional variation is more complex than described in this semi-empirical model, a reasonable agreement with the experimental data under a variety of conditions was observed [101-104]. Indeed, the calculated crosslink density continuously increases in proportion to the concentration of SilSoy in the IPN (Figure 3. 44).





As mentioned above, the high dependency of the crosslink density on the SilSoy concentration is directly related to the relatively large number of silanol crosslink sites in this phase compared with much fewer numbers of the terminal silanols on the PDMS phase. This increase in the crosslink density is essentially the mirror-image of the swelling behavior shown in Figure 3. 43.

It should further be emphasized that although the network is not uniform, both phases (e.g. the silylated soybean oil and PDMS) are participating in the network. If only one of these phases was cured, semi-IPNs would have been formed where one component is interlocked (but not covalently linked) to the other component. Obviously, the identical cure reactions in this case lead to full IPNs.

3.5.2.4. Mechanical properties

The effects of composition on the mechanical properties of the IPNs are shown in Figure 3. 45and the main properties are presented in Table 3. 5. As indicated from the gel-swell measurements, the sample containing 80 wt.% silylated soybean oil and the sample composed of only cured silylated soybean oil (no PDMS) had a high degree of crosslinks and thus were too brittle to accurately determine the tensile properties. The sample composed of cured PDMS (no silylated soybean oil) was found to have similar elastomeric properties to those previously reported in the literature [105].



Figure 3. 45 Stress–strain of IPNs composed of different concentrations of silylated soybean oil/PDMS. (a) 0/100, (b) 20/80, (c) 40/60, and (d) 60/40

The tensile strength and the initial modulus increased as the concentration of the silylated soybean oil fraction in the IPN increased while the elongation at break decreased. These changes were undoubtedly related to the high crosslink density of the silylated soybean oil matrix as described earlier. It is interesting to note that, generally, the elongation at break of semi-IPNs does not decrease drastically as the crosslink density is increased when compared to full IPNs[59]. This trend is simply due to the fact that the un-crosslinked phase in the semi-IPN acts as a plasticizer or a polymeric filler and exhibits higher mobility compared to full IPNs where the crosslinking of both phases restrict the mobility of the network.

In the current silvlated soybean oil/PDMS IPNs the elongation at break is drastically reduced as the silvlated soybean oil concentration is increased, clearly indicating that this phase is an integral part of the network. Similarly, as the concentration of the soft PDMS phase is decreased, the modulus and the tensile strength of the sample are higher.

Table 3. 5 Mechanical properties of IPNs composed of different concentrations of silylated

Soy/PDMS		Tensile Strength	Elongation
[wt./wt.]	E [MPa]	[MPa]	at break [%]
0/100	2.5 ±0.3	0.03 ± 0.01	656 ± 0.3
20/80	4.2 ±0.4	0.03 ± 0.01	496 ± 0.4
40/60	3.8 ±0.2	0.05 ± 0.01	302 ± 0.2
60/40	10.3 ±0.2	0.04 ± 0.01	5 ± 0.2
80/20*		-	H

soybean oil/PDMS

It follows from the mechanical properties that the crosslinked silylated soybean oil acts as a high modulus resin-like component and the lightly crosslinked PDMS as a ductile matrix. Apparently, the relatively low molecular weight of the triglycerides before crosslinking (e.g. roughly 900) contains roughly one silyl group per fatty acid residue that leads to a free chain length of ~300 between crosslinks. Furthermore, since each grafted silane contains three silanols and each of these silanols is available to form short disiloxanes crosslinks, the distance between crosslinks is very short resulting in a rigid matrix with very low elongation. In contrast, the PDMS phase is composed of high molecular weight linear polymers that are well above the Tg and the polymer chains are tied to the network only at the chain-ends. This type of structure is expected to lead to a matrix that is highly flexible and elastomeric. Thus, useful compositions in this series are IPNs composed of high concentrations of PDMS as the continuous phase leaving the rigid silvlated sovbean oil as a discontinuous, dispersed phase.

3.5.2.5. Thermal properties

The thermal properties of cast IPN films were investigated by DSC (Figure 3. 46). The melting temperature of PDMS (T_{m1}) was observed at -43°C and slightly increased as the concentration of the silvlated soybean oil was increased.



Figure 3. 46 DSC of IPNs composed of different concentrations of silylated soybean oil/PDMS. (a) 0/100, (b) 20/80, (c) 40/60, (d) 60/40, and (e) 80/20

The enthalpy of this melting transition was inversely proportional to the concentration of the silylated oil and decreased from 16.53 J/g for PDMS to 3.18 J/g for the sample composed of only 20% PDMS, respectively (Table 3. 6). This increase in the melting point and decrease of the enthalpy indicate a lower organization of the PDMS chains due to the formation of the network. Furthermore, a small but noticeable melting temperature (T_{m2}) was observed related to the saturated fatty acid content in the soybean oil triglycerides. The melting temperature was not affected by the composition of the IPN but the enthalpy of this melting transition was directly proportional to the concentration of the silylated soybean oil in the IPN. Apparently, the

saturated fatty acids do not participate in the network since the grafting of the silane only occurs onto the double bonds of the unsaturated fatty acids. Consequently, the saturated fatty acids act as "dangling ends" and are free to crystallize. This general phenomenon has been observed previously in various other IPNs where a net decrease in the chains mobility was noted due to close interactions (e.g. physical crosslinks and chain entanglements) between the phases in the micro-domains[10, 67].

oil/PDMS

Soy/PDMS [wt./wt.]	T _{m1} [°C]	$\Delta \mathbf{H}_1 \left(\mathbf{J} / \mathbf{g} \right)$	T _{m2} [°C]	$\Delta \mathbf{H}_2 (\mathbf{J/g})$
0/100	-47.3	16.53	-	-
20/80	-16 9	12.27	-6 10	1.671
20/80	-40.9	12.27	-0.19	1.071
40/60	-46.0	8.98	2.83	1.572
60/40	-44.2	7.36	4.99	2.454
80/20	-44.9	3.18	8.14	4.848

 Table 3. 6 Thermal properties of IPNs composed of different concentrations of silvlated soybean

Т

Since the siloxanes linkages are well known for their high bond strength and thermal stability to homolytic cleavage, it was interesting to evaluate the thermal stabilities of the IPNs as a function of the siloxanes content. It was surprising to note from the TGA data (Figure 3. 47) that the onset temperature of degradation of the PDMS network (containing no silvlated oil) was only 315°C, much lower than one would expect from crosslinked PDMS rubber. Apparently, the presence of DBTDL, which is a known reversible condensation catalyst, caused premature degradation via rearrangement of a ring-chain equilibrium[106].



Figure 3. 47 TGA of IPNs composed of different concentrations of silylated soybean oil/PDMS. (a) 0/100, (b) 20/80, (c) 40/60, (d) 60/40, (e) 80/20, and (f) 100/0

It was also unexpected to note that the silylated soybean oil thermogram (Figure 3. 47, trace f) consists of two degradation modes, the first at 131°C and the second at 374°C. The higher degradation temperature is a typical degradation temperature of soybean oil. Presumably, the lower degradation temperature is related to the redistribution reaction that results in free fatty acid methyl esters at elevated temperatures.

It is important to note that the degradation of simple blends (no IPN) of PDMS and soy oil does not depend on the relative concentration of each component in the blend. Thus, the degradation temperature of each component in the blend will not be affected by the other component in the blend. The TGA results (Figure 3. 47) indicate that extensive grafting, crosslinking, and interpenetration are responsible for the observed thermal behavior of the IPNs.

3.5.2.6. Calculations for the Biobased Content of Latex IPNs

The total percentage of biobased content in the system is calculated as the ratio of the total percentage of biobased carbon to the organic carbon available into the sample [6, 99, 107].

Conventionally, biobased content in the system is calculated based on the elemental analysis of the sample as described in ASTM D6866 [6, 8]. However, the biobased content of these IPNs was calculated based on its composition. During calculations, inorganic carbon like calcium carbonate is excluded from the calculations and in the ASTM D6866 method for measuring biobased carbon content, any carbonate present is removed before measuring the biobased carbon content [8, 99].

For our systems, as described in the methods, the biobased content for the developed IPNs was calculated based on the equation. Since the IPNs developed is mainly only a two component system and the biobased carbon content, total carbon content and the mass of the each component into the IPNs is exactly known. For an example, for the IPNs containing 20 wt.% PDMS and 80 wt.% SilSoy.

The number of carbons present in the soybean oil are 57 and the silylated soybean oil participating into the crosslinking has the total 59 carbon atoms present per repeat unit. The total mass of the repeat unit of SilSoy participating in the crosslinking is calculated to be 997 kg/ kmole. Similarly, the PDMS repeat unit has the molecular weight of 74 kg/ kmole and the total carbons present in the repeat unit is 2. Substituting these values into the equation, we get,

$$BCC_{SilSoy} = \frac{57}{59} \times 100 = 96.61\%$$

OCC_{SilSoy} =
$$\left(\frac{59 \times 12}{997}\right) \times 100 = \frac{71.01 \, kg \, of \, C}{100 \, kg \, of \, Mat.}$$

 $W_{SilSoy} = 0.8$

And,

BCC_{PDMS} =
$$\frac{0}{2} \times 100 = 0\%$$

OCC_{PDMS} = $(\frac{2 \times 12}{74}) \times 100 = \frac{32.43 \text{ kg of C}}{100 \text{ kg of Mat.}}$

 $W_{PDMS} = 0.2$

Thus, the biobased content of the IPNs containing 20 wt.% PDMS and 80 wt.% SilSoy is 86.71%.

The biobased content for the IPNs calculated is given below in the table 3.7 –

IPN Composition			Biobased
	SilSoy	PDMS	Content [%]
1	20	80	34.18
2	40	60	57.33
3	60	40	74.06
4	80	20	86.71

Table 3. 7 Calculated biobased content for Latex IPNs

3.5.3. CONCLUSIONS

A series of IPNs were prepared by combining and curing latexes of silylated soybean oil and PDMS. Since the oil phase of both latex particles contained terminal silanol groups, a common crosslinking mechanism based on the condensation of silanols to form siloxanes crosslinks. Some crosslinks were induced while in emulsion (e.g. intra-particle crosslinks) and led to partially crosslinked oil particles while still suspended in emulsion. Upon evaporation of the water phase and casting films, additional inter-particle crosslinks took place, which interlocked the two phases together and prevented gross phase separation. The properties of the IPNs were affected by the relative concentration of each phase, however, no gross phase separation was observed and the silylated soybean oil phase was intimately mixed with the PDMS phase at all concentrations. The morphology was examined by SEM and appeared as a dispersion of the minor component in the continuous matrix of the major component when the concentration of each phase was radically different. However, when the concentrations of the silylated soybean oil and the PDMS were roughly similar, bicontinuous morphology was observed. In these cases diffused particles that closely adhere to each other were observed.

Although both phases were crosslinked to form full IPNs, the crosslink density of each phase was different. The crosslink density of the IPNs was determined using a model developed and it was correlated with the swelling behavior observed for the IPNs. The silylated soybean oilcomponent was characterized by a low gel fraction and a low swell ratio indicating regions of high crosslinks but other regions that contain no crosslinks. The PDMS component was characterized by a high gel ratio and high degree of swelling indicating a more uniform crosslink structure due to the relatively long chain lengths between crosslinks. This unusual behavior was still explained by the model developed and thus, the actual crosslink density of these IPNs was calculated and quantified. This uneven morphology and crosslink distribution affected the mechanical properties of the cast films. At low concentrations of silylated soybean oil (high PDMS content) the films were elastomeric with relatively high elongation and moderate tensile strength. Conversely, at high concentration of silylated soybean oil (low PDMS content) the cast films were resin-like materials with high modulus and low elongation at break.

DSC and TGA results indicate that extensive grafting, crosslinking, and interpenetration affect the thermal properties of these IPNs. However, the thermal decomposition temperatures of

the IPNs were lower than soybean oil or typical silicone rubber. This lower degradation stability is most likely due to the DBTDL redistribution catalyst left in the system that caused transesterification and formation of free fatty acid methyl ester.

These new IPNs provide convenient, one-package, crosslinked water-based coatings derived from PDMS and soybean oil. The coatings can be used as high release liners, low friction materials or as a general protective coating.

CHAPTER 4: INTERPENETRATING POLYMERS NETWORKS DERIVED FROM OLIGOMERIZED SOYBEAN OIL AND POLYDIMETHYLSILOXANE

4.1. INTRODUCTION

The broad definition of an Interpenetrating Polymer Network (IPN) is a material containing two or more immiscible components that have been crosslinked in the presence of each other to form entangled (interpenetrated) networks [2]. Due to the intimate mixing and crosslinks, no gross phase separation takes place and IPNs appear as homogeneous materials to the naked eye. It was found that the morphology of such intimate entanglements of the two or more immiscible polymeric networks can lead to interesting physical properties that cannot be achieved by grafting, blending or other mixing techniques. Currently, products derived from IPNs find applications include false teeth to ion-exchange resins, adhesives, high impact plastics, thermoplastics, vibration-damping materials (for outdoor, aircraft and machinery applications), high temperature alloys and medical devices [3]. Based on the method of synthesis, IPNs can be classified into the following three categories: (A) Latex IPNs (LIPN) whereby the formation of the interpenetrating networks is achieved by emulsion polymerization; (B) Simultaneous Interpenetrating Networks (SIN) whereby the first polymer is mixed with a monomer of a second polymer along with the initiator and a crosslinking agent allowing it to polymerize and crosslink inside the swollen first polymer and (C) Sequential IPN (SIPN) whereby two polymers are mixed either in a solution or in the bulk and then crosslinked in presence of each other [108].

Since it is difficult to incorporate triglycerides into polymeric systems because of the inherent branched structure of the triglycerides, the relatively long chain length of the fatty acids and the inherent incompatibility of these biobased materials with many synthetic polymers [52], an efficient approach would be to use the IPN technology [53, 54]. Indeed, several IPNs have been described in the literature that contain either plant oils or oil based polymers. Some
examples include IPNs that were derived from combining hard and brittle alkyds with soft and flexible poly (butyl methacrylate) polymers [59]. These IPNs exhibit better physical properties than each of their individual components. Similarly, IPNs of alkyd and polyurethane (also known as uralkyds) that were prepared by solution casting followed by air vulcanization have also been reported. These IPNs produced tough coatings with superior abrasion and chemical resistance [57, 58]. Several examples of castor oil IPNs with acrylates or polyesters have also been reported and these IPNs showed better mechanical and physical properties than the individual components [10-15]. Other IPNs have been prepared from functionalized vernonia oil [60], lesquerella oil, crambe oil, and linseed oil (as well as their epoxidized derivatives) with polystyrene and polyacrylics[18, 20, 23, 61-63]. Most of the previous IPN work with triglycerides involved preparing a homogeneous solution of the triglycerides with the desired monomer, then polymerizing and crosslinking as phase separation occurred. Thus, the morphology of the resulting IPN is generally a function of the kinetics of the phase separation. In this work, we wish to report a different approach where the IPNs are prepared from solution of silvlated polymerized soybean oil and PDMS.

Recently, it was shown that the incorporation of refined unsaturated vegetable oils as a biobased feedstock is advantageous for several industrial applications such as printing inks, lubricants and general coating applications [109]. However, it was reported that for best results in these applications, high viscosity oils are preferred instead of the native triglycerides. One method to increase the viscosity (and the molecular weight) of soybean oil is the ring opening process of epoxidized soybean oil with anhydrides and alcohols [110, 111]. Microwave irradiation of soybean oil has been reported to increase the viscosity of the oil and has been used to develop biobased lubricants [112]. Another approach was to use air plasma for the

polymerization of soybean oil [113]. Alternatively, anthraquinone has been used as a thermal catalyst for the oligomerization of soybean oil in the development of printing inks [114, 115]. In fact the bodying of triglycerides under thermal conditions is an established technique that has been studied extensively and is protected by several patents. One typical example describing the use of heat and catalysts to increase the rate of the dimerization reaction of alkene is described by Lozada*et al*[115]. A semi-continuous process for the bodying of drying oil has also been reported which clearly established that the triglycerides react to yield highly branched structures during this heat bodying process [116]. This thermal polymerization of oils and fats is characterized by increased viscosity products and the formation of high molecular weight polymers with interesting physicochemical properties [64, 109].

Although there are numerous IPNs containing PDMS with a variety of synthetic polymers, there are no IPNs of PDMS and natural oils or fats [38, 64-67]. The published silicone containing IPNs display clear microphase separation and multiphase domain structures because of the inherent immiscibility of PDMS with most organic polymers. Many of these IPNs have interesting and useful properties because of the high chain flexibility, low surface energy, high thermal stability, and low Tg of the polysiloxane chain. Previously, we described an example of IPNs containing triglycerides and siloxane polymers that were prepared by the latex method and were useful for various coating applications [47]. The latex IPN method is a convenient method for the generation of IPNs from low viscosity materials. However, it is difficult to prepare latexes from the high viscosity substances. Thus an alternative approach is needed if one is to use high viscosity (bodied) oils.

In this work we wish to describe the preparation of IPNs derived from silylated oligomerized SOSO and PDMS prepared from a solution containing a common crosslinking

agent. Upon casting films crosslinking takes place to yield IPNs where the two phases are intimately mixed and crosslinked. These IPN resins can be used as high release liners, low friction materials, or as convenient one-package protective coatings.

4.2. EXPERIMENTAL

4.2.1. Materials

LowSat[®] soybean oil was kindly supplied by Zeeland Farm Services (Zeeland, MI). Silanol terminated dimethylsiloxane oligomers with a viscosity of 50,000 cSt (Weight average molecular weight of 115,000 gm/ mole) and vinyltrimethoxysilane (VTMS) were purchased from Gelest Inc. (Morrisville, PA). Anthraquinone, toluene, dibutyltindilaurate (DBTDL) and 2,5-Bis (tert-butylperoxy)-2,5-dimethylhexane (Luperox[®]101) peroxide, were purchased from Sigma-Aldrich (St. Louis, MO).

4.2.2. Equipment and Characterization

Thermogravimetric analyses (TGA, TA instruments, USA, Q50) were obtained by heating samples (approximately 10 mg) from room temperature (RT) to 550°C at 10°C/min under a nitrogen atmosphere.

Differential scanning calorimetry (DSC, TA instruments, USA, Q20) data were obtained by first heating a sample (approximately 5 mg) under a nitrogen atmosphere to 250°C to erase any thermal history, then cooling to -70°C at 10°C/min followed by heating to 250°C at 10°C/min.

The mechanical properties (stress-strain) were measured at the temperature range of -50°C to 300°C using a Dynamic Mechanical Analyzer (DMA, TA instruments, USA, Q800) with a constant shear of 0.01 N and frequency of 100µm applied on the sample. The DMA sample was equilibrated for 5 minutes at -50°C and then ramped up to 300°C with the heating rate of 3°C/min.

The molecular weight was determined by gel permeation chromatography (GPC) equipped with a refractive index detector (Shimadzu, Japan, RID-10A) using tetrahydrofuran as mobile phase. The calibration was performed with polystyrene standards.

The viscosity was measured using a Brookfield digital viscometer (Brookfield Engineering, USA, LVDV-E) equipped with spindle LV-1 (61) suitable for a viscosity range of 15 - 20,000 cPs.

The extent of crosslinking was determined by measuring the gel and swell ratios of cast films as described in the ASTM D2765-11 [71].

Scanning electron microscopy (SEM, Japan Electron Optics Laboratories, Japan, JEOL-6400V) was used to study the morphology of fractured surfaces. A fresh surface was obtained by fracturing the specimen in liquid nitrogen. The fractured surface was fixed with 1% osmium tetroxide (OsO4) solution to stain the unsaturation of the oligomerized soybean oil. Each image was observed under a backscatter electron detector for better resolution and contrast. Thus, the silylated oligomerized soybean oil in these images appears as lighter shade domains while the polysiloxane appears as darker shade domains.

4.2.3. Oligomerized Soybean Oil

In a typical synthesis of oligomerized soybean oil, low saturated soybean oil and anthraquinone catalyst were heated as described in the literature [114]. Briefly, one mole (894 grams) of soybean oil was mixed with 45 grams of anthraquinone (~5% w/w) in a 2L Parr reactor. Inert atmosphere was maintained in the reactor by purging it with nitrogen for 10

minutes. The content was then heated to 330°C under constant stirring for three hours. Once the reactor was cooled down, the oligomerized soybean oil that was obtained was dissolved in hexane (800 grams) and filtered to remove the catalyst. The filtrate was then heated to 68°C to strip the hexane.

4.2.4. Silylation of Oligomerized Soybean Oil

Silylation of the oligomerized soybean oil was accomplished by heating 886 grams of this oil with 296 grams (2 moles) of VTMS at 225°C under constant stirring in a Parr reactor. The reaction was monitored by TGA to follow the extent of grafting and was terminated after 3 hours once all the oligomerized soybean oil had been grafted. The silylated oligomerized soybean oil (SOSO) was dissolved in THF and was analysed by GPC to determine the molecular weight and molecular weight distribution.

4.2.5. Preparation of SOSO/PDMS IPNs

In a typical experiment, SOSO and silanol terminated PDMS were combined and dissolved in toluene. A series of such solutions containing different concentrations of PDMS and SOSO were prepared (Table 4. 1). DBTDL (1% w/w) condensation catalyst and 1% w/w of water as a hydrolyzing agent were added to each solution. The solutions were stirred well for a few minutes to ensure complete mixing and then about 10 grams of each solution were poured into Teflon coated petri-dishes. Upon evaporation of the solvent, homogeneous IPN films were obtained.

	PDMS	Continuous Phase	Dispersed Phase	Domain Size of the		Crosslink
SOSO				Dispersed Phase [µm]		Density
				Mean	STD	[x10 ⁻⁸ mol/cm ³]
20	80	PDMS	SOSO	25.58	15.78	6.98
40	60	SOSO	PDMS	19.72	4.23	24.00
50	50	SOSO	PDMS	14.30	10.45	51.04
60	40	SOSO	PDMS	8.21	6.43	128.09
80	20	SOSO	PDMS	4.37	2.12	904.66

 Table 4. 1 IPNs prepared from SOSO and PDMS

4.2.6. Calculation of Biobased Content of the Solution IPNs

The biobased content of the IPNs was calculated based on the calculations mentioned in the literature [99].

The total biobased content for the multi-component system was calculated using the following equation:

$$BCC_{prod.} = \frac{\sum (W_n \times BCC_n \times OCC_n)}{\sum (W_n \times OCC_n)}$$

Where,

 $BCC_n = Biobased$ Carbon Content of the nth component.

 $OCC_n = Organic Carbon Content of the nth component.$

 $W_n = Mass of the nth component.$

4.3. RESULTS AND DISCUSSION

Oligomerization of the soybean oil under our experimental conditions increased the viscosity of the oil from 30 cPs to 5760 cPs (weight average molecular weight of 281,000 gram/ mole). This oil was then combined with silanol terminated PDMS in toluene at different relative concentrations. A small amount of water was added to hydrolyze the methoxy groups of the grafted silane (Figure 4. 1) and the resulting silanols were allowed to condense and form the desired network (Figure 4. 2).



Figure 4.1 Hydrolysis of methoxysilane groups grafted onto SOSO



Figure 4. 2 Condensation of silanols groups to yield siloxane crosslinks between silanol terminated PDMS and SOSO

It should be emphasized that under these conditions siloxane linkages between SOSO and PDMS can be obtained by silanol condensation as well as siloxane linkages between two SOSO molecules or two PDMS molecules. The ultimate outcome is a crosslinked network held together by siloxane crosslinks that prevents any gross phase separation of the oligomerized soybean oil and the polysiloxane oil.

4.3.1. Morphology

The morphology of cast IPN films composed of different compositions is shown in Figure 4. 3 and illustrates a typical IPN microphase separation. In this series of SEM images, the PDMS phase appears as dark areas and the SOSO phase containing the unsaturated fatty acids that were stained with osmium tetroxide as the bright areas. It is apparent that the overall size of the dark areas increases in direct proportion to the concentration of PDMS in the IPN.

Furthermore, the shape of the dispersed SOSO particles generally appears as elongated oval particles while the PDMS particles appear to be more symmetrical spherical particles. This apparent difference in the shape of the dispersed phases could be related to the crosslinking process and the mechanical properties of the SOSO phase where a higher silanol concentration and a more rigid network was obtained while the solutions were stirring before casting. In contrast, the spherical shape of the PDMS dispersed phase is most likely related to the low crosslink density of this phase and the flexible nature of the PDMS polymer.



Figure 4. 3 SEM images of IPNs with different ratio of SOSO/PDMS. (A) 80/20 (B) 60/40, (C) 50/50, (D) 40/60 and (E) 20/80

Of particular interest is the phase inversion between the continuous SOSO phase and the dispersed PDMS phase (Figure 4. 3E). It is clear from this image that somewhere between 60-80 wt.% PDMS the morphology changes to form a continuous PDMS phase where SOSO particles are dispersed in it. This apparent phase inversion is also reflected in the other properties of the IPNs as discussed below.

4.3.2. Crosslink density

The degree of crosslinking was determined by measuring swell and gel fractions at different compositions (Figure 4. 4and Figure 4. 5, respectively). In these experiments, equilibrium swell ratio (Q) was calculated using equation 1:

where, W_{P0} is the initial weight of the sample, W_S is the weight of the solvent in the swollen sample at equilibrium, d_P the density of the sample and d_S is the density of the solvent.

The gel fraction (G) was calculated using equation 2:

$$G = \frac{W_P}{W_{P0}} \times 100$$
 (2)

where, W_P is the weight of the dried sample after all the extractable sol was removed during swelling.



Figure 4. 4 Gel fractions [G] of IPNs composed of different concentrations of SOSO and PDMS



Figure 4. 5 Swell Ratio [Q] of IPNs composed of different concentrations of SOSO and PDMS

The degree of swell is related to the free chain length between crosslinks and the interaction of the solvent with the polymer chains. Thus, low crosslink density usually indicates a high degree of swelling and a low gel fraction. However, it is apparent from our data that plots of both the swell ratio and the gel fraction are inversely proportional to the concentration of SOSO in the IPN. These observations where high swell ratio is associated with high gel fraction is highly unusual and not commonly observed in polymeric systems [47]. One likely explanation could be related to the non-homogeneous structure of the IPN where the relatively high molecular weight PDMS fraction is lightly crosslinked (e.g. it consists of only terminal silanol groups per polymer) whereby the SOSO fraction contains multiple crosslink sites (e.g. multiple grafted silanols per molecules). Thus, at low SOSO concentrations where the IPNs consist of primarily PDMS, a relatively loose network is obtained due to the limited number of crosslink sites. As the concentration of SOSO is increased, micro-phase separation containing regions of high crosslink density are obtained next to PDMS regions that are characterized with lower crosslink density. Subsequently, both the gel fraction and the swell ratio decrease. It should

further be emphasized that both components (e.g. the SOSO and PDMS) are crosslinked and participate in the network. If only one of these phases was crosslinked to yield semi-IPNs, the gel fraction would be directly proportional to the concentration of the crosslinked phase but the swell ratio would have been inversely proportional to the concentration of this phase.

A thermodynamic approach was used to correlate the cellular domain size in IPNs with the crosslink density [49, 50, 101]. A model was developed in chapter 2 based on the Donatelli's equation to predict the crosslink density of IPNs (equation 3). The main variables in this derivation are the average diameter of the domains of the dispersed phase, the composition of polymers and the interfacial energy between the two polymer phases. Since the two polymers are inherently incompatible, some micro-phase separation occurs even when the polymers are intimately mixed as depicted in Figure 4. 3.

$$n = \frac{2\gamma W_B}{RTD_B \left[\frac{1}{(1-W_B)^{2/3}} - \frac{1}{2}\right]} \quad \dots \dots \dots (3)$$

where, n_A : crosslinking density in moles/cm³

W_B: weight fraction of the dispersed phase

- *R*: Gas constant in J/mole
- T: Temperature in K

 D_B : The domain diameter of the dispersed phase in cm

 γ : Interfacial energy between the two phases in dynes/cm

It was concluded that, in general, the size of the cellular phase domain in IPNs is inversely proportional to the crosslink density. Although, it was realized that the compositional variation is more complex than described in this semi-empirical model, a reasonable agreement with the experimental data under a variety of conditions was observed [101-104]. Indeed, the calculated crosslink density continuously increases and reaches a plateau in proportion to the concentration of SOSO in the IPN (Figure 4. 6). As mentioned above, the high dependency of the crosslink density on the SOSO concentration is directly related to the relatively large number of silanol crosslink sites in this phase compared with much fewer numbers of the terminal silanols on the high molecular weight PDMS phase. This increase in crosslink density is essentially the mirror-image of the swelling behavior shown in Figure 4. 5.



Figure 4. 6 Crosslink density as calculated from Eq. 3 as a function of SOSO concentration in

the IPN

4.3.3. Thermal Properties

DSC plots (Figure 4. 7) indicate a melting transition at -45°C independent of the IPN composition, a small melting peak around 5°C and a relatively large transition around 175°C that

is clearly dependent on the IPN composition. It is apparent that the area under the low temperature peak is directly proportional to the concentration of PDMS (Figure 4. 7) and undoubtedly is therefore due to melting of the polysiloxane phase [47].

The magnitude of the broad melting peak that is observed at around 5°C is directly proportional to the concentration of the SOSO phase. Thus, it is most likely due to the melting of the saturated fatty acids in the triglycerides. These saturated fatty acids are not affected by the grafting reaction and are known to melt around this temperature. The area under the relatively large peak around 175°C is directly proportional to the SOSO concentration in the IPN (Figure 4. 8). Further analyses of this transition indicate that it is related to the curing reaction in these IPNs as it is not present upon repeated heating/cooling cycles.



Figure 4. 7 DSC curves of IPNs with different ratio of SOSO/PDMS. (A) 80/20; (B) 60/40; (C)

50/50; (D) 40/60 and (E) 20/80



Figure 4.8 Curing of SOSO in IPNs as a function of their composition

Thus, upon heating a sample above this transition and then cooling it down, no apparent peak is observed (Figure 4. 9). No traces of this peak were observed after subsequent heating and cooling cycles even when the sample was allowed to equilibrate for a substantial period of time between these cycles. It was therefore concluded that this transition could not have been related to melting or crystallization and is simply due to an incomplete cure when the IPN samples are allowed to cure at room temperature.



Figure 4. 9 Representative DSC plots of IPN (SOSO/PDMS 80/20) indicating the disappearance of the peak at 175°C upon repeated heating/cooling cycles

4.3.4. Mechanical Properties

DMA curves of IPNs prepared with different concentrations of SOSO and high molecular weight silanol terminated PDMS are shown in Figure 4. **10**. The data indicate the presence of two transitions; a major peak below 0°C (Tan δ_1) and a smaller peak at around 125°C (Tan δ_2). The low temperature transition appears as a multiple peak consisting of one maximum just below 0°C and another maximum that is inversely proportional to the SOSO concentration in the IPNs (Figure 4. 11).



Figure 4. 10 Tan δ observed as a function of temperature for different ratio of SOSO/PDMS (A)

80/20; (B) 60/40; (C) 50/50; (D) 40/60 and (E) 20/80



Figure 4. 11 Maximum Tan δ_1 as a function of IPN composition

It is apparent that at low SOSO concentration (20 wt. %) in the IPN, a symmetric, almost Gaussian peak is observed. However, at high SOSO concentration (80 wt. %) or in films prepared from just SOSO, this peak is much broader and uneven. It is therefore most likely associated with the crystal transition of the saturated fatty acids in the SOSO that did not participate in the silane grafting reaction and are free to crystallize around this temperature range.

Surprisingly, the area under this tan δ transition indicates that it reaches a maximum value in IPNs containing 60 wt. % SOSO (Figure 4. 12). This unexpected maximum is directly related to the phase inversion observed in the morphology (Figure 4. 3) where at low SOSO concentration the continuous phase is the low modulus PDMS. In comparison, the morphology of IPNs composed of more than 50 wt. % SOSO is characterized by high modulus, high crosslinked SOSO phase, which is the continuous phase while the PDMS phase consists of discontinuous particles suspended in the SOSO matrix.



Figure 4. 12 The maximum of Tan δ value observed at the initial peak

The position of the peak at 125°C (tan δ_2) appears to be independent of the IPN composition. However, the area under this peak depends on the composition of the IPN (Figure 4. 13) and the maximum area appears to be related to the phase inversion observed earlier. Apparently, here again the change from a relatively "soft" continuous PDMS matrix to a more "rigid" continuous SOSO phase corresponds to this change in the mechanical properties.



Figure 4. 13 Tan δ_2 observed at 131°C as a function of IPN composition

4.3.5. Calculations for the Biobased Content of the Solution IPNs

The total percentage of biobased content in the system is calculated as the ratio of the total percentage of biobased carbon to the organic carbon available into the sample [6, 99, 107]. Conventionally, biobased content in the system is calculated based on the elemental analysis of the sample as described in ASTM D6866 [6, 8]. However, the biobased content of these IPNs was calculated based on its composition. During calculations, inorganic carbon like calcium carbonate is excluded from the calculations and in the ASTM D6866 method for measuring

biobased carbon content, any carbonate present is removed before measuring the biobased carbon content [8, 99].

For our systems, as described in the methods, the biobased content for the developed IPNs was calculated based on the equation. The IPNs developed are of only a two component system and the biobased carbon content, total carbon content and the mass of the each component into the IPNs is exactly known. The biobased content calculated for the series of IPNs made from SOSO and PDMS by solution IPN method is shown in the table 4.2.

IPN	Biobased		
	SOSO	PDMS	Content [%]
1	20	80	37.05
2	40	60	61.07
3	50	50	70.17
4	60	40	77.91
5	80	20	90.36

 Table 4. 2 Calculated biobased content for Solvent - Based IPNs

4.4. CONCLUSIONS

A series of IPNs was prepared by crosslinking high molecular weight silanol terminated PDMS and oligomerized, silylated soybean oil (SOSO) from toluene solution. The crosslinks in these IPNs are derived from condensation reactions of the silanols in both phases that form siloxane linkages. These siloxanes crosslinks lead to a network that consists of siloxanes linkages between PDMS and SOSO as well as siloxanes linkages within each of these components. The morphology of these IPNs appears to be homogeneous to the naked eye but consists of "seaisland" microphase separation whereby one phase is suspended as small particles in the other continuous phase. Phase inversion is observed when the concentration of the suspended phase is increased beyond 50 wt. %. Due to the difference in the concentration of silanols in each of the IPN components, the network is not homogeneous and each phase consists of different crosslink densities. The SOSO phase is characterized by a low gel fraction and a low swell ratio due to the relatively high concentration of silanols and high numbers of crosslinks. The PDMS phase is characterized by a much lower crosslink density since this high molecular weight polymer contains only terminal silanols and thus relatively long chain lengths between crosslinks.

The thermal and mechanical properties of cast films were affected by the composition and the morphology of these IPNs with a major shift around the phase inversion point. The incorporation of silanol functional groups on the oligomerized soybean oil provides a convenient approach to prepare new compositions from inherently incompatible components. Similar to other IPNs, these partial biobased compositions could be useful as protective coatings.

CHAPTER 5: INTERPENETRATING POLYMERS NETWORKS DERIVED FROM SILYLATED SOYBEAN OIL AND WATER SOLUBLE POLYSILOXANES

5.1. INTRODUCTION

An Interpenetrating Polymer Network (IPN) is defined as a material containing two or more immiscible components that have been crosslinked in the presence of each other to form entangled (interpenetrated) networks [2]. Due to the intimate mixing, chain entanglements supplemented by crosslinks prevent gross phase separation such that IPN films appear homogeneous to the naked eye. These intimate entanglements of the two or more polymeric phases lead to a unique morphology and interesting physical properties that cannot be achieved by either phase alone or by simple mixing. Currently, products derived from IPNs find many diverse applications including false teeth, ion-exchange resins, adhesives, high impact plastics, thermoplastic materials, vibration-damping compositions used for outdoor, aircraft and machinery applications, high temperature alloys and medical devices [117].

The branched structure of the triglycerides as well as the relatively long chain length of the fatty acids and the inherent incompatibility of triglycerides with many synthetic polymers make it difficult to incorporate soybean oil (and other triglycerides of vegetable oils) with other polymers [52]. Consequently, using an IPN approach with selected oils was used before as an efficient method to obtain apparent homogeneous compositions [53, 54]. For example, interesting IPNs were prepared from flexible poly (butyl methacrylate) with rigid alkyd resins [59]. It was found that these IPNs exhibited better physical properties than each of their individual components. Similarly, IPNs prepared from alkyd resin and polyurethane (also known as uralkyds) were found to yield tough coatings with superior abrasion and chemical resistance [57, 58]. Castor oils were widely used in various IPNs due to the availability of the hydroxyl group which could be used for crosslinking. Thus, IPNs of polyacrylates with castor oil or polyesters with castor oil were prepared and were shown to have better mechanical and physical properties than the individual components [10-15]. In addition to castor oil, other functionalized oils (vernonia oil [17], lesquerella oil, crambe oil, and linseed oil) were also used in IPNs with polystyrene and polyacrylics[18, 20, 23, 62, 63]. Most of the previous IPN work with triglycerides involved preparing a homogeneous solution of the triglycerides with specific monomers, then polymerizing and crosslinking it as phase separation occurred. Thus, the morphology of these IPNs is generally a function of the phase separation kinetics in these systems.

Among the IPNs containing hydrophilic polymers, polyvinyl alcohol has been explored widely including biotechnical and biomedical applications due to its inherent non-toxicity, hydrophilicity and biocompatibility [118]. It has been used in drug delivery matrices [119] or in the tablet formation [120]. Chitosan has been investigated for preparing IPNs by crosslinking it with gluteraldehyde[121, 122]. Polyacrylic acid has also been investigated in the development of IPNs for drug delivery systems and hydrogels [123]. IPNs have also been developed from poly(methacrylic acid) and poly(*N*-isopropylacrylamide) for pH and temperature sensitive hydrogels [124].

Polydimethylsiloxane (PDMS) has been incorporated with other synthetic polymers [38, 64, 65, 67] to form IPNs. These IPNs exhibited typical microphase separation and multiphase structures because of the inherent immiscibility of PDMS with most organic polymers. Many of these IPNs have had interesting properties because of the low surface energy, high thermal stability and high chain flexibility that are characteristic to the polysiloxane chain. Although there are a large number of silicone-containing IPNs reported in the literature, IPNs from triglycerides and hydrophilic polysiloxanes have not been reported.

Silicone polymers, primarily PDMS, have also been employed in various controlled release applications due to their hydrophobic nature [125] for anesthetics [126] and other pharmaceutical products [127-129] as well as in controlled release of fertilizers (CRFs). The most widely used CRF systems are derived from polyolefins such as polyethylene that is usually blended with a high permeability polymer such as ethylene-vinyl-acetate to control the nutrient release [130], crosslinked resins such as alkyd resins (Osmocote) or polyurethane resins (Polyon, Multicote etc.) [130, 131]. However, these CRF systems are not biodegradable or self-erodible and are left in the ground after the fertilizer is released.

We have developed a series of IPNs from emulsions of biobased-silylated soybean oil and hydrophilic polysiloxanes. Uniform crosslinked films were obtained after evaporation of the water phase and the mechanical, thermal and swelling properties of these films were studied. The hydrophilic polysiloxanes provides flexibility and high moisture permeability whereby the silylated soybean oil provides rigidity and hydrophobicity. The crosslink linkages in these IPNs are primarily composed of Si-O-C linkages, which are susceptible to hydrolysis yielding control release systems that disintegrate in the environment in which the release rate is controlled by the extent of the hydrolysis.

5.2. DEVELOPMENT OF HYDROPHILIC POLYSILOXANES FROM 3-AMINOPROPYLMETHYLDIETHOXYSILANE AND ETHYLENE CARBONATE FOR APPLICATIONS IN IPNS

5.2.1 BACKGROUND

Polydimethylsiloxane (PDMS) has been used in a wide variety of applications including contact lenses[132], microfluidic devices [132-134], micro-contact printing technology [135, 136], and drug delivery systems [132, 137-139]. The use of PDMS in this impressive number of applications is directly related to the many attractive features of polysiloxanes. High oxygen

permeability, non-toxicity and biocompatibility, high stability toward heat and chemicals, low crystallization temperature, moldability, high flexibility, good optical transparency and ease of sealing with other materials are a few notable examples. These desirable properties are derived from the siloxane backbone covalent bonds that are longer than carbon-carbon bonds, are more flexible and have higher thermal stability [132]. However, wider use of this polymer is limited due to the inherent hydrophobicity of PDMS where the methyl groups shield the siloxane linkages. The hydrophobic nature of PDMS is most notable in applications where cells and proteins are irreversibly deposited onto the surface of PDMS. Indeed, the hydrophobic nature of PDMS is a key factor limiting the applications of polysiloxanes as biocompatible polymers [140]. Consequently, much effort has been directed toward surface modification of polysiloxanes in order to render them hydrophilic, improve their biocompatibility and increase the wettability.

Typical surface modifications include plasma [132, 133, 141], ultraviolet irradiation followed by the ozone exposure [142, 143] and introduction of polar groups by corona discharges [144]. Unfortunately, none of these surface treatments proved useful and effective due to the so called "hydrophobic recovery", where the methyl groups rearrange back onto the polymer-air interface, and physical damage of the surface leading to cracks and crazes. It is apparent that there is a need to enhance the hydrophilic nature of polysiloxanes by treatments other than these physical surface treatments.

One chemical modification method to enhance the hydrophilic properties is to graft copolymerize PDMS with polyethers[145, 146]. Indeed, this chemical modification was extensively used to prepare silicone surfactants. It commonly involves ethoxylation or propoxylation of the polymer backbone, using ethylene oxide or propylene oxide and requires special equipment and facilities due to the toxic and explosive nature of the oxides [145]. Alternatively, PDMS containing methyl hydrogen siloxanes segments have been hydrosilylated with vinyl terminated hydrophilic polyethers[147]. The copolymers products of this reaction are useful as surfactants and their hydrophilic-lipophilic balance (HLB) is directly related to the composition. Obviously, increasing the polyether content in the copolymers leads to lower polysiloxane content and a loss of other polysiloxane inherent properties.

Introduction of various hydrophilic functional groups such as quaternary ammonium salts (QAS) or hydroxyalkyl groups have also been used to enhance the hydrophilic properties of polysiloxanes [148, 149]. Other techniques include introduction of amine-functional groups or carboxylic groups that form soluble salts in aqueous acid solutions [150-152] or alkaline solutions, respectively. Introduction of halogen functional groups such as chlorides or bromides have also been utilized in an attempt to render the polysiloxane surface more hydrophilic. These techniques, however, are highly dependent on the pH and the molecular weight of the polymer.

Our studies indicate that polysiloxanes containing multiple hydroxyl groups can impart high hydrophilicity to polysiloxanes and even render them completely soluble in water. Furthermore, the solubility of these carbinol functional polysiloxanes is independent of pH and the molecular weight of the polymers. Here, we wish to describe the preparation method and some key properties of these carbinol functional polysiloxanes. The polymerization process is fairly simple and does not require expensive catalysts, solvent or special equipment. Furthermore, the same process can be used to prepare copolymers with controlled surface properties[153].

5.2.1. EXPERIMENTAL METHODS

5.2.1.1. Materials

3-aminopropyldiethoxymethylsilane (APDES) was purchased from Gelest Inc. (Morrisville, PA, USA). APDES was kept under a nitrogen atmosphere to prevent hydrolysis by atmospheric moisture. Ethylene carbonate (anhydrous, 99%) and hexamethyldisiloxane (HMDSO) were purchased from Sigma Aldrich (St. Louis, MO, USA). All reagents were used as received unless specified otherwise.

5.2.1.2. Equipment and Characterization

¹H NMR spectra were recorded on a 500 MHz NMR spectrometer (Varian Unity Plus, Varian Associates Inc., California, USA) using the deuterated methanol (CD₃OD-D) solvent peak as an internal standard. Differential scanning calorimetry (DSC; Q20, TA Instruments, Delaware, USA) data were obtained by first heating a sample under a nitrogen atmosphere to 100°C, then cooling to -70°C at 10°C/min followed by heating to 200°C at 10°C/min. Thermogravimetric analyses (TGA; Q50, TA Instruments, Delaware, USA,) were obtained by heating samples from room temperature (RT) to 550°C at 10°C /min under a nitrogen atmosphere. The viscosity was measured using a Brookfield digital viscometer (DV-E, Brookfield Engineering, Massachusetts, USA) at RT. IR Spectra were recorded on Shimadzu FTIR (IRAffinity-1, Shimadzu Co., Tokyo, Japan) equipped with a single reflection MIRacle ATRsystem (PIKE Technologies, WI, USA,). Contact angle measurements were performed using Kruss Contact Angle Equipment (DSA100, Kruss USA, NC, USA) by placing a drop of 4 µL onto the film surface and measuring the contact angle over time using a static contact angle measurement method. Water was used as a solvent for the measurements. The sessile drop method was employed to analyze the contact angle. The mechanical properties (e.g. stress-strain curves) were measured at RT using a Universal Testing Machine (SFM-20, United Calibration Corp. and United Testing Systems Inc., California, USA) according to ASTM D638. The tensile tests were performed at a strain rate of 0.1 inch /min and in all cases at least five specimens of each sample were tested and the average value was recorded. Paper coating samples were prepared using a manual Single Roll Lab Coater (E-BC12M1, Euclid Coating Systems Inc., MI, USA). A scanning electron microscope (SEM, 6610LV, Japan Electron Optics Laboratories, Japan) was used to study the morphology of fractured surfaces of the paper-coated samples. A fresh surface was obtained by fracturing the specimen in liquid nitrogen followed by coating it with 20 nm gold.

5.2.1.3. Preparation of Hydrophilic Polysiloxanes (HPPS)

Typical polymerization consisted of first hydrolyzing APDES (191 grams, 1 mole) with 36g (2 moles) of distilled water and 1.4g (.009 moles) of hexamethyldisiloxane (HMDSO). HMDSO was used as a chain terminator to control the molecular weight of the polymer. The reaction was carried out in a 500 mL round bottom flask under constant mechanical stirring for 3 hours at room temperature until a homogeneous clear solution was obtained. This solution was then heated to 100°C for two hours to strip excess water and ethanol to complete the polymerization (Figure 5.1). Samples were taken periodically during the reaction and reacted with a calculated amount of ethylene carbonate to obtain the desired hydroxyl functionality. The progress of the polymerization reaction was followed by measuring the viscosity as a function of time (Figure 5.2).



Figure 5. 1 Preparation of carbinol functional polysiloxane (HPPS) from 3-

aminopropylmethyldiethoxysilane



Figure 5. 2 Viscosity as a function of polymerization time

The amine functional polysiloxane that was obtained was placed in a 2L Parr reactor and was purged with nitrogen to ensure an inert atmosphere. Ethylene carbonate (88 grams, 1 mole) was then added at 80°C and the mild exothermic reaction temperature was maintained at this temperature by adjusting the addition rate of ethylene carbonate. Once all ethylene carbonate was added, agitation was continued for an hour to ensure complete reaction.

Aqueous solutions were then prepared by dissolving 280 grams of HPPS in 280 grams (50% w/w solution) in the Parr reactor. In order to ensure complete solubility, the temperature of

the reactor was increased to 150°C under constant stirring for two hours. After cooling, a clear solution of the polymer was obtained. Films were cast by pouring the polymer solution (11 grams) in 90mm Teflon lined petri-dishes and allowing the films to dry at room temperature and constant relative humidity for at least 3 days before measuring their physical properties.

5.2.2. RESULTS AND DISCUSSION

The polymerization reaction was followed by periodically removing a sample, reacting it with ethylene carbonate and determining the viscosity. The change in viscosity as a function of time is given in Figure 5.2. It is apparent from these data that the viscosity increased exponentially during polymerization as typically observed for condensation polymerization and then leveled off as equilibrium polymerization was attained. It should be emphasized that the rapid increase in the viscosity is not only the result of the increase in the molecular weight but also due to hydrogen bonding of the pendent hydroxyl groups. Thus, a very high apparent viscosity (e.g. 405,000 cPs) was observed for the polymer that was designed to have a molecular weight of 25,000 gm/ mole by the HMDS end-group.

This polysiloxane is composed of hydroxyl functional group on every silicon atom. Thus, the hydroxyl value of the carbinol functional silane (from the reaction of APDES with ethylene carbonate) was found to be 201 mg KOH/ gram. It continuously increases and then levels off as a function of the molecular weight of the polymer at 270 mg KOH/ gram (Figure 5.3).



Figure 5. 3 Calculated hydroxyl value as a function of molecular weight.



Figure 5. 4 ¹H NMR of HPPS

The final structure of the polymer was confirmed by ¹H NMR as shown in Figure 5.4. The resonance peak at 0.1 ppm corresponds to the methyl group attached to the silicon atom. The resonance peaks at 0.5 ppm, 1.55 ppm and 3.05 ppm correspond to the propyl linkage attached directly to the silicon atom. The appearance of the peak at the chemical shift of 3.65 ppm and at 4.05 ppm corresponds to the methylene linkages from the reaction of ethylene carbonate and indicates the conversion of the amine to carbamate with a terminal hydroxyl group [153]. This resonance clearly indicates that the amino-functional polymer has been reacted to completion with ethylene carbonate to produce the desired pendent carbinol groups. The resonance peaks at 2.5 ppm and 3.55 ppm correspond to ethanol that was obtained as a by-product in the hydrolysis of APDES. This is also confirmed by FTIR analysis of the polymer product.



Figure 5. 5 FTIR spectra of A: APDES and B: HPPS

FTIR further confirmed the structure of the polysiloxane as can be seen by comparing the spectrum of APDES (Figure 5.5A) to the final product after reaction with ethylene carbonate (Figure 5.5B). The spectrum of APDES is characterized by Si-O-CH₂CH₃ vibration at 950 cm⁻¹ and a characteristic vibration between 1100 cm⁻¹ and 1200 cm⁻¹alkoxysilane[154]. The final product after reaction with ethylene carbonate (Figure 5.5B) clearly shows a characteristic carbamate vibration at 1650 cm⁻¹ and hydroxyl stretching peak at 3400 cm⁻¹ as well as a strong absorption of Si-O-Si between 1000 cm⁻¹ - 1100 cm⁻¹ confirming the formation of the siloxane

backbone. Furthermore, the carbonate peak at 1750 cm⁻¹ is missing, indicating that all ethylene carbonate had reacted.

5.2.2.1. Mechanical Properties

Figure 5.6 represents the typical stress-strain curve of HPPS where the stress continuously increases in proportion to the strain until the sample fails with a tensile strength of 180 KPa and ultimate elongation of 25% (Table 5.1). It should be emphasized that the test films were not covalently crosslinked or reinforced with silica as is the usual case with PDMS. Instead, the films are held together by hydrogen bonds alone. Furthermore, the test films were equilibrated at 27% relative humidity prior to the measurements and contained water although they appeared soft, dry to the touch and tack-free.



Figure 5. 6 Stress-strain curve of HPPS equilibrated at RT and 27% humidity

Properties	Average	Standard Deviation	
Tensile Stress [Kpa]	180.0	110.0	
Elongation at Break [%]	24.7	3.4	
Young's Modulus [Kpa]	410.0	130.0	
Toughness [Kpa]	52.0	23.0	

 Table 5. 1 Representative mechanical properties of HPPS.

5.2.2.2. Contact Angle

The contact angle measurements (Figure 5.7) clearly show the hydrophilic character of HPPS. It is apparent that the initial contact angle was fairly low (96°) and continuously decreased with time period and reached a lower plateau of only 40° after 500 seconds. Apparently the interaction of water with the surface of the polymer reduced the contact angle over time. Undoubtedly, the relatively low observed contact angle is due to the availability of the hydroxyl group on each silicon atom as well as to the polar nature of the carbamate side chain group.



Figure 5. 7 Water contact angle of HPPS as a function of time.

It is interesting to note that poly(vinyl alcohol) (PVOH) that also contains hydroxyl functional group on each monomer unit has a similar equilibrium contact angle with water (45°) at room temperature [155]. The presence of multiple hydroxyl groups, hydrogen bonding and the film forming ability of HPPS with its low contact angle, the ability to swell in water and the rubbery, elastic appearance can be used for various biomedical, pharmaceutical and industrial applications [156]. Furthermore, as is the case with PVOH that contains a few acetyl groups left unhydrolyzed that greatly impact the properties of this polymer, copolymerization of HPPS with a few dimethylsiloxane units can have a considerable effect on the properties. One such example is the water solubility of these polymers; PVOH composed of less than 88% acetate hydrolysis in not completely soluble in cold water. However, as extent of hydrolysis is increased, the water solubility decreases such that the fully hydrolyzed PVOH is characterized by high water resistance. However, these hydrolyzed grades of PVOH are readily soluble in hot water whereby fully hydrolyzed high molecular weight PVOH requires high temperatures under pressure to

ensure complete solubility [157]. The water solubility of HPPS is similar and complete solubility requires heating this polymer to 120°C under pressure.

5.2.2.3. Paper Coatings

Films of HPPS cast from water solutions are transparent and elastomeric even in the absence of crosslink or reinforcing agents. The ability of HPPS to form films was demonstrated by coating it on printing paper. SEM images (Figure 5.8) show a uniform coating on the paper with no apparent defects or "fish-eyes". As a paper coating, HPPS offers chemical resistant to oils, greases, waxes, organic solvents and, similar to PVOH, higher resistance to water than starch.

HPPS can be a suitable candidate for textile sizing and fiber coating as the flexible siloxane backbone can impart smoothness to the fiber while the hydrogen bonding due to the pendent hydroxyl groups can provide reinforcement to the fiber structure. Other potential applications could include thermoplastic elastomers and specialized adhesives. Unlike PVOH with its relatively high Tg that reduces its effectiveness as an adhesive at low temperatures, HPPS remained elastomeric well below RT. Further copolymerization of HPPS with PDMS can open the door to new surfactants with well-defined HLB.


Figure 5.8 SEM images of A: Uncoated Paper and B: Paper coated with HPPS



Figure 5. 9 DSC of A: PDMS, B: HPPS with bonded water and C: Dried HPPS

5.2.2.4. Thermal Properties

The thermal properties of cast films from aqueous solutions were analyzed by DSC and compared with PDMS (Figure 5.9A). As expected, the melting temperature of PDMS was

observed at -43°C with no other thermal transitions through the experimental temperature range. In contrast, no melting point in the temperature range of -70°C to 200°C was observed for HPPS. A large endothermic transition (200.6 J/g) was observed at 170°C related to loss of the bound water from the polymer. It is apparent that this transition is due to bound water simply by keeping the sample at 175°C for 15 minutes and repeating the test (Figure 5.9C). It is clear from the data that the endothermic peak at 175°C, which corresponds to the evaporation of water, disappeared in the DSC histogram indicating that this polymer has no thermal transitions in this temperature range.



Figure 5. 10 TGA of HPPS equilibrated at 27% relative humidity

The presence of bound water in HPPS was further confirmed by TGA analysis (Figure 5.10) where about 21% of weight loss was observed from 140°C to 200°C. No further degradation was observed in HPPS thereafter until 360°C. In comparison the bound water in PVOH evaporates at around 120°C leaving the polymer very brittle above this temperature [158]. It has been reported [159, 160] that PVOH degradation consists of dehydration followed by

chain scission and cyclization reaction. In contrast, after the initial elimination of bound water from HPPS the siloxane polymer remained stable to 360°C with no apparent degradation of the Si-O-Si linkages. Furthermore, similar to other polysiloxanes degradation at elevated temperatures yielded about 40% residual silica.

5.2.3. CONCLUSIONS

Hydrolysis and condensation of 3-aminopropylmethyldiethyxysilane followed by polymerization with hexamethyldisiloxanes as a chain terminator was used to obtain well defined polysiloxane. Subsequent reaction of the amines in this polysiloxane with ethylene carbonate led to pendant carbamate with terminal hydroxyl groups. The structure of this polysiloxane was confirmed by ¹H NMR, FTIR. The high degree of hydrogen bonding was directly related to the high viscosity of this polymer. The extremely low contact angle with water confirmed the hydrophilic nature of the polymer. The DSC and TGA data indicate the presence of bound water associated with the hydroxyl functional groups. No thermal transitions were observed over a wide temperature range and the high ultimate degradation temperature was directly related to the high thermal stability of the polysiloxane backbone. The mechanical properties and the ability of this polymer to form high quality coatings indicate that this polymer could be used for specialized coating applications as anti-graffiti coatings and possible replacement for PVOH in some applications.

This hydrophilic polysiloxane polymer synthesized as described in this section was then incorporated in Interpenetrating Polymer Networks (IPNs) derived from silylated soybean oil.

5.3. DEVELOPMENT OF IPNS FROM CARBINOL FUNCTIONAL HYDROPHILIC POLYSILOXANES (HPPS) AND SILYLATED SOYBEAN OIL (SILSOY)

5.3.1. BACKGROUND

Interpenetrating Polymer Networks were prepared from emulsions of silylated soybean oil (SilSoy) and hydrophilic polysiloxanes (HPPS). The process of synthesis of HPPS has been discussed in the section 1 of chapter 5 and the process of synthesis of SilSoy has been discussed in Section 2 of chapter 3. These materials were used for the synthesis of IPNs and has been discussed in this section.

5.3.1. EXPERIMENTAL METHODS

5.3.1.1. Materials

Low-saturated soybean oil was supplied by Zeeland Farm Services (Zeeland, MI, USA). Vinyl trimethoxysilane (VTMS) and 3-aminopropyldiethoxymethylsilane (APDES) were purchased from Gelest Inc. (Morrisville, PA, USA). Ethylene carbonate (anhydrous, 99%), hexamethyldisiloxane (HMDSO), sodium dodecyl sulfate (SDS), dibutyltindilaurate (DBTDL), dimethylsufoxide (DMSO) and 2,5-Bis (tert-butylperoxy)-2,5-dimethylhexane peroxide (Luperox101[®]) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All reagents were used as received unless specified otherwise.

5.3.2.2. Equipment and Characterization

The equipment used for the synthesis and the analysis of the IPNs have been described in the section 1 and section 2 of the chapter 3. The equipment not used before are described in this section.

The morphology of the IPNs was observed using a Scanning Electron Microscope (SEM, JEOL 6610LV, Japan Electron Optics Laboratories, Japan). A fresh surface of the sample was

obtained by fracturing the specimen in liquid nitrogen. The fractured surface was fixed with 1% osmium tetroxide (OsO4) solution to stain the unsaturation of the soybean oil. Each image was observed under backscatter electron detector for better resolution and contrast. Thus, the silylated soybean oil appears as a brighter shade (white phase), while the polysiloxanes appears as a darker phase.

The extent of crosslinking was determined by measuring the gel and swell ratios of cast films using DMSO as a solvent following ASTM D2765-11. In all cases, the samples were allowed to swell at RT for 120 hours before they were removed and dried at RT to a constant weight.

5.3.2.3. Silylation of Soybean Oil (SilSoy) and emulsification

The silylated soybean oil was prepared according to a procedure described previously [47]. Briefly, low-saturated soybean oil (600 g), VTMS (306 g), and Luperox 101 (6 g) were added to a 2L Parr reactor (Parr Instrument Company, USA, PARR 4841). The reactor was purged with nitrogen to maintain an inert atmosphere and was then heated to 280°C for 8 hours to graft the VTMS onto the soybean oil by the "Ene reaction" as shown in Figure 5.11. The product contained an average of 2.4 moles of grafted silane per triglyceride.



Figure 5. 11 Silylation of unsaturated fatty acids in soy oil triglycerides with VTMS by the "Ene reaction."

The silylated soybean oil (900 g) thus obtained was homogenized with SDS (22.5 g) in a laboratory homogenizer (Manton-Gaulin, USA, model No. 15MR) at 53 MPa (two passes) to produce a stable emulsion containing 45% solids. Upon aging, methoxysilanes hydrolyzed to form silanol (Si-OH) functional groups attached to the soybean oil. The silylated soy oil emulsion was then neutralized to a pH of 10 using a 1M KOH.

5.3.2.4. Synthesis of Hydrophilic Polysiloxanes (HPPS)

Synthesis of HPPS has been described in the section 1 of this chapter (5.1). Same procedure was used for developing HPPS to incorporate into the IPNs.

5.3.2.5. Preparation of SilSoy-HPPS IPNs

Different IPN compositions (Table 5.2) were prepared by adjusting the amounts of HPPS dissolved in the aqueous phase and the oil phase in the SilSoy emulsions. In all cases, the mixed emulsions were stable with no apparent signs of coagulation or creaming. Films from these

emulsions were then cast on Teflon lined petri dishes and the water was allowed to evaporate at RT. Films thus obtained appeared uniform with no apparent gross phase separation.

5.3.2.6. Environmental degradation

The film (1 sq. inch) made from an IPN containing 50% silylated soybean oil (SilSoy) and 50% hydrophilic polysiloxane (HPPS) was kept in four different solutions each having a different pH and maintained at room temperature. The containers were sealed to avoid evaporation of water. The time required for the disintegration of the films was observed periodically and noted and mentioned in Table 5.3.

SilSoy	HPPC	Domain Size [µ]		Crosslink density
Content [wt. %]	Content [wt. %]	Mean	STD	[x10 ⁻⁸ moles/ cm ³]
10	90	3.11	1.21	121.46
20	80	3.86	1.65	169.77
30	70	12.45	4.39	67.89
40	60	13.11	7.61	72.93
50	50	13.98	10.01	71.17

Table 5. 2 IPNs prepared from SilSoy and HPPC

Table 5. 3 Effect of pH on film degradation

рН	Time [hours]
2	4
4	10
10	10
12	4

5.3.2.7. Calculation of Biobased Content of the IPNs

The biobased content of the IPNs was calculated based on the calculations mentioned in the literature [99].

The total biobased content for the multi-component system was calculated using the following equation:

$$BCC_{prod.} = \frac{\sum (W_n \times BCC_n \times OCC_n)}{\sum (W_n \times OCC_n)}$$

Where,

 $BCC_n = Biobased Carbon Content of the nth component.$

 $OCC_n = Organic Carbon Content of the nth component.$

 $W_n = Mass$ of the nth component.

5.3.3. RESULTS AND DISCUSSION

The extent of VTMS grafting onto the unsaturated fatty acids in the soybean oil triglycerides grafting was determined by TGA [47]. Excess VTMS that was not grafted was not removed since hydrolysis and condensation of all the siloxy groups, whether grafted or free, would lead to silanols that would participate in the IPN network.



Figure 5. 12 Schematic structure of IPNs derived from SilSoy and HPPC

It should be emphasized that the cast IPN films are crosslinked by stable siloxanes (Si-O-Si) and hydrolytically less stable siloxy (Si-O-C) linkages as shown schematically in Figure 5.12. Specifically, the grafted silanols on the SilSoy can condense to form the stable siloxane bonds between the SilSoy molecules in the IPN. Siloxy bonds are formed in the condensation of the grafted silanols on the SilSoy with the pendant carbinol of HPPS. It is well known that, although these Si-O-C linkages between the SilSoy phase and the HPPS phase are hydrolytically unstable, they maintain intimate mixing and prevent gross phase separation of the IPN structure under dry conditions. It should be emphasized that HPPS does not participate in the network via siloxane linkages since the terminal groups of this polymer are trimethylsiloxanes that were obtained by the addition of HMDSO to control the polymer molecular weight.

5.3.3.1. Morphology

The morphology of cast IPN films with different ratios of HPPS to SilSoy is observed as a typical IPN structure consisting of microphase separation of one component in the other as shown schematically in Figure 5.12. Actual SEM images are shown in Figure 5.13 where the HPPS phase is the dark area and the SilSoy, containing the unsaturated fatty acids that were stained with OsO₄, appears as bright phases.

It is apparent that the overall size of the white areas increases in direct proportion to the concentration of the SilSoy in the IPN. Furthermore, HPPS is the continuous phase in these IPNs whereby SilSoy is always the dispersed phase in this range of compositions. At low concentrations of SilSoy, the two phases are intimately dispersed but as the SilSoy concentration is increased the phase separation becomes more distinct (Figure 5.13). The actual shape of the particles in the dispersed phase is affected by the degree of crosslinking and the mechanical properties. Here, the SilSoy phase is composed of higher concentration of silanol and shorter free chain length between crosslinks than HPPS and therefore it contributes to the rigidity as a reinforcing filler within the rubbery HPPS matrix.

The morphology of these IPNs is dominated by two types of crosslinks, hydrolytically stable siloxanes (Si-O-Si) and hydrolytically less stable siloxy (Si-O-C) covalent bonds. The siloxanes crosslinks are obtained by condensation of the silanol groups in the SilSoy phase and the siloxy crosslinks are obtained by condensation between silanols in SilSoy and carbinols in HPPS.



Figure 5. 13 SEM images of IPNs with different ratio of SilSoy/HPPC. (A) 10/90, (B) 20/80, (C) 30/70, (D) 40/60 and (E) 50/50.

Thus, only the siloxy crosslinks hold the two incompatible phases together as the interpenetrating network and prevent gross phase separation between the two phases. It follows that increasing the content of SilSoy leads to more silanol – silanol condensation and the formation of a more rigid and hydrolytically stable network. Furthermore, since the free chain length between crosslink in this phase is relatively short, higher concentrations of SilSoy (or smaller concentrations of HPPS) would be expected to increase the siloxanes crosslink density. Indeed, it is observed (Figure 5.13) that the size of SilSoy particles dispersed in the HPPS continuous matrix increases in proportion to the concentration of SilSoy (Table 5.2).

5.3.3.2. Crosslink density

The degree of crosslinking was determined by measuring swell and gel fractions at different compositions (Figure 5.14 and 5.15, respectively). In these experiments, equilibrium swell ratio (Q) was calculated using Equation 1:

$$Q = \frac{W_{P0} / d_P + W_s / d_s}{W_{P0} / d_P} \quad \text{(Eq. 1)}$$

where, W_{P0} is the initial weight of the sample, W_S is the weight of the solvent in the swollen sample at equilibrium, d_P the density of the sample and d_S is the density of the solvent.

The gel fraction (G) was calculated using Equation 2:

$$G = \frac{W_P}{W_{P0}} \times 100$$
 (Eq. 2)

where, W_P is the weight of the dried sample after all the extractable sol was removed during swelling.

The degree of swell is related to the polymer-solvent interactions as well as the free chain length between crosslinks. Thus, low crosslink density usually indicates a high degree of swelling and a low gel fraction. It is apparent from our data that the swell ratio is directly proportional to the SilSoy content (Figure 5.14) while the gel fraction is inversely proportional to the concentration of SilSoy in the IPN (Figure 5.15). Typically, low crosslink density is characterized by high swell ratio and low gel fraction. The swell-gel data indicate that increasing the concentration of the SilSoy phase in this series of IPNs led to higher swell ratio and lower gel fraction, which apparently indicate lower crosslink density networks. This is of the formation of Si-O-C crosslinkes that are formed as a result of the additional SilSoy in the system.



Figure 5. 14 Swell ratio of IPNs with different concentrations of SilSoy/HPPC



Figure 5. 15 Gel swell ratio of IPNs with different concentrations of SilSoy/HPPC

A thermodynamic approach (Eq. 3) that was used to correlate the crosslink density from the dispersed domain size [49, 50, 101]in these IPNs indicates that the swell-gel data do not provide a complete description of the networks.The main variables in the derivations of Equation 3 are the crosslink density, the molecular weight of the polymers and the interfacial energy between the two polymer phases in the IPN. Since the two polymers are inherently incompatible, it is expected that some micro-phase separation occurs even when the polymers are intimately mixed with each other as depicted in Figure 5.13. Thus, the crosslink density is given by:

$$n_A = \frac{W_B \left[\frac{2\gamma}{RTD_B} - \frac{1}{M_B}\right]}{\left[\frac{1}{(1 - W_B)^3} - \frac{1}{2}\right]} \quad (Eq. 3)$$

where, n_A : crosslinking density in moles/cm³

 W_B : weight fraction of the dispersed phase

R: Gas constant in J/mole

T: Temperature in K

 D_B : The domain diameter of the dispersed phase in nm

 γ : Interfacial energy between the two phases in dynes/cm

M_B: Molecular weight of polymer B. (For crosslinked polymers, $M_B = \infty$)

Equation 3 predicts that the size of the dispersed phase domain is inversely proportional to the crosslink density. Although, it has been realized that the compositional variation is more complex than the correlation predicted by this semi-empirical model, a reasonable agreement with the experimental data under different conditions was observed for several IPNs [101-104].

We observed that the calculated crosslink density continuously decreased and was inversely proportional to the concentration of SilSoy in the IPN (Figure 5.16). It was unexpected from the added silanols in the system and the subsequent large number of Si-O-Si crosslink sites in this phase. The gel-swell data support the crosslink analysis from Donatelli's equation as the change in the particle size is inversely proportional to the crosslink density. However, the experimental error in this correlation is relatively high due to: (1) The dispersed particles are not spherical and thus their precise area is difficult to determine, and (2) Some hydrolysis of the Si-O-C linkages had occurred during swelling, which effectively reduced the overall crosslink density. It is apparent however that the general trend is a decrease in the crosslink density of the IPNs with the addition of the SilSoy.



Figure 5. 16 Crosslink density as calculated from the Donatelli Equation as a function of SilSoy concentration in the IPN

5.3.3.3. Mechanical Properties

Typical stress-strain curves from different compositions of SilSoy/HPPS IPNs are shown in Figure 5.17 and the derived ultimate properties, modulus and toughness are listed in Table 5.4. It is apparent that the tensile strength and the initial modulus increased as the concentration of the silylated soybean oil fraction in the IPN increased while the elongation at break decreased.

 Table 5. 4 Selected mechanical properties of IPNs made from different ratios of SilSoy and HPPC.

Duomouter	Silylated Soybean Oil Content [%]				
Property	10%	20%	30%	40%	50%
Tensile Stress [Mpa]	0.22 ± 0.07	0.21 ± 0.10	0.47 ± 0.12	0.27 ± 0.11	0.19 ± 0.05
Elongation at Break [%]	21.56 ± 2.31	18.21 ± 2.04	19.95 ± 1.47	8.52 ± 1.02	3.260 ± 0.18
Young's Modulus [Mpa]	0.46 ± 0.05	0.74 ± 0.11	1.01 ± 0.04	1.41 ± 0.07	3.00 ± 0.06
Toughness [Mpa]	0.075 ± 0.017	0.086 ± 0.006	0.281 ± 0.054	0.122 ± 0.031	0.019 ± 0.002



Figure 5. 17 Stress – Strain Curves of IPNs with different SilSoy/HPPC ratio (A) 10/90, (B) 20/80, (C) 30/70, (D) 40/60 and (E) 50/50 obtained at room temperature and 27% humidity.

These changes were undoubtedly related to the high crosslink density of the SilSoy matrix as described earlier. It is interesting to note that generally the elongation at break of semi-IPNs does not decrease drastically as the crosslink density is increased when compared to full IPNs [59]. This trend is simply due to the fact that the uncrosslinked phase in the semi-IPN acts as a plasticizer or a polymeric filler and exhibits higher mobility compared to full IPNs, where the crosslinking of both phases restrict the mobility of the network. In the current SilSoy/HPPS IPNs, the elongation at break is drastically reduced as the SilSoy concentration is increased, clearly indicating that this phase is an integral part of the network. Similarly, decreasing the concentration of the soft HPPS phase led to higher modulus and the tensile strength.

The mechanical data confirms that the SilSoy phase acts as a high modulus component due to the relatively low molecular weight of free chain-length between crosslinking (approximately 1000 gm/mol) and each crosslink is composed of tri-functional silanols (derived from trimethoxy grafted silanes). The flexible nature of the polysiloxane backbone in HPPS provides ductility to the IPNs. However, the free pendant hydroxyl group on each silicon atom still contributes to the mechanical properties by hydrogen bonding in this polymeric phase.

5.3.3.4. Environmental degradation

The ratio of the stable siloxane (Si-O-Si) crosslinks, derived from condensation of silanols to the hydrolytically unstable siloxy (Si-O-C) crosslinks derived from the condensation of pendant carbinols with grafted silanols, determines the environmental stability of these IPNs. Therefore, understanding the factors affecting the environmental degradation is important for potential applications of these IPNs in the environment.

Hydrolysis of Si-O-C bonds is well known [98, 161] and occurs by nucleophilic attack of the oxygen contained in water on the silicon atom in either acid or base pH. The data in Table 5.3 clearly show that these IPNs degrade in the environment and the degradation rate is proportional to the pH. The environmental degradation is not the biodegradation. It is the degradation of IPNs due to the cleavage of Si-O-C covalent bonds by hydrolysis. This controlled hydrolysis can be utilized in various control release applications including release of fertilizers, pesticides or herbicides to the soil or in general control release of active ingredients. A comprehensive review of the factors affecting the hydrolysis of Si-O-C bonds [104] indicates that this hydrolysis depends on the environmental conditions (e.g. pH, temperature, moisture content) as well as the presence of any catalysts and steric effects due to the nature of the leaving group. Although many of these studies were concerned with short alkoxy groups (e.g. methoxy, epoxy, etc.) it was shown that steric factors, due to the alkyl chain length and degree of branching, exert the greatest effect on the hydrolytic stability under any conditions [162, 163].

Under basic conditions water dissociates to produce nucleophilic hydroxyl anions in a rapid first step. The hydroxyl anion then attacks the silicon atom via a S_N2 -Si mechanism in which the hydroxyl group displaces the alkoxy group with inversion of the silicon tetrahedron [100, 164]. It was noted that because the silicon atom acquires a formal negative charge under these conditions, the hydrolysis is quite sensitive to inductive as well as steric effects.

In comparison, acid-catalyzed mechanisms are preceded by protonation of the OH or OR substituents attached to the silicon atom. The protonation leads to lower electron density of the silicon, making it more electrophilic and thus more susceptible to attack by water. Thus, when a water molecule attacks, it acquires a partial positive charge and the positive charge of the protonated alkoxide is correspondingly reduced making the alcohol a better leaving group. Here

too, the hydrolysis rate is increased by substituents which reduce steric crowding around silicon atom.

As described in detail[165], initial depolymerization of high molecular weight siloxanes is caused by soil hydrolysis of the siloxane bonds to yield organosilanol terminated oligomers. These organosilanols are evaporated into the atmosphere and are then oxidized there by hydroxyl radicals to benign silica, water, and CO₂.

5.3.3.5. Thermal Properties

DSC plots (Figure 5.18) indicate a small melting peak around 5°C and a relatively large transition around 160°C that is clearly dependent on the IPN composition. The magnitude of the broad melting peak that is observed at around 5°C is directly proportional to the concentration of the SilSoy phase. This melting temperature remains unchanged by the composition of the IPN but the enthalpy of this melting (the area under the peak) appears to be directly proportional to the concentration of the concentration of SilSoy in these IPNs.



Figure 5. 18 DSC of IPNs with different ratio of SilSoy/HPPC (A) 10/90, (B) 20/80, (C) 30/70,

(D) 40/60 and (E) 50/50.

This thermal transition is undoubtedly due to the saturated fatty acids that do not participate in the crosslinking. Consequently, these saturated fatty acids act as "dangling ends" and are free to crystallize [47]. This is a common phenomenon in IPNs containing triglycerides and a net decrease in the mobility of the chains was reported in these IPNs because of close interactions (e.g. physical crosslinks and chain entanglements) between the phases in the microdomains[10, 67].

SilSoy Content [wt. %]	Peak Position [°C]	Heat of Reaction [J/gm]
0	148.94	200.4
10	160.52	185.6
20	151.07	140.4
30	161.21	153.0
40	153.76	116.8
50	153.38	90.6

Table 5. 5 Thermal Properties of IPNs with different SilSoy/HPPC compositions

The area under the relatively large peak around 160°C is directly proportional to the SilSoy concentration in the IPN (Figure 5.18). The peak position and the enthalpy of this endothermic peak are listed in Table 5.5 for different IPN compositions. It is clear from these data that the enthalpy of this transition is directly proportional to the HPPS concentration and continuously decreased as the HPPS concentration in the IPN was decreased. However, the temperature of this transition was independent of the composition. Further investigations clearly indicated that this peak corresponds to bound water molecules closely interacting with the carbinol groups in the HPPS phase. This bound water could be removed from the IPNs only at elevated temperatures (above 140°C), much higher than the boiling temperature of water under

normal atmospheric conditions as shown by TGA analysis (Figure 5.19). The TGA results of IPNs with different compositions is similar to the IPN data shown indicating the presence of water tightly bound to the carbinol groups in HPPS.



Figure 5. 19 Representative TGA of IPNs composed of different ratios of SilSoy/ HPPS (A) 0/ 100 and (B) 50/ 50

5.3.3.6. Calculations for the Biobased Content of the IPNs

The total percentage of biobased content in the system is calculated as the ratio of the total percentage of biobased carbon to the organic carbon available into the sample [6, 99, 107]. Conventionally, biobased content in the system is calculated based on the elemental analysis of the sample as described in ASTM D6866 [6, 8]. However, the biobased content of these IPNs was calculated based on its composition. During calculations, inorganic carbon like calcium carbonate is excluded from the calculations and in the ASTM D6866 method for measuring biobased carbon content, any carbonate present is removed before measuring the biobased carbon content [8, 99].

For our systems, as described in the methods, the biobased content for the developed IPNs was calculated based on the equation. The IPNs developed are of only a two component system and the biobased carbon content, total carbon content and the mass of the each component into the IPNs is exactly known. The biobased content calculated for the series of IPNs made from SOSO and PDMS by solution IPN method is shown in the table 5.6.

IPN	l Composit	Biobased	
	SilSoy	HPPS	Content [%]
1	10	90	16.61
2	20	80	30.76
3	30	70	42.96
4	40	60	53.59
5	50	50	62.93

 Table 5. 6 Calculated biobased content for the IPNs

5.3.4. CONCLUSIONS

A series of IPNs was prepared from latexes of silylated soybean oil (SilSoy) using aqueous solutions containing hydrophilic polysiloxane (HPPS) at different concentrations. Upon casting films and evaporation of the water phase, stable siloxane (Si-O-Si) and hydrolytically unstable siloxy (Si-O-C) crosslinking were obtained that prevented gross phase separations between the silicone and the soy phases.

The morphology of these IPNs analyzed by SEM indicated a dispersion of SilSoy domains within the continuous HPPS phase. The extent of the crosslink density was analyzed by gel-swell data and compared with a semi-empirical model derived from the size of the dispersed domains. It was observed that the overall extent of crosslinking was inversely proportional to the

concentration of SilSoy in the IPNs but increasing the concentration of this phase led to a higher concentration of the hydrolytically unstable siloxy (Si-O-C) linkages. This morphology of the IPNs was affected by the crosslink density which impacted the mechanical properties of cast films. At low concentrations of SilSoy oil (high HPPS content), the films were elastomeric with relatively high elongation and moderate tensile strength whereby at high SilSoy concentrations, the cast films were characterized by relatively high modulus and low elongation at break.

Due to the different nature of the crosslinking in these IPNs, cast films can be degraded in the environment by combination of water and pH. This degradation by hydrolysis of Si-O-C linkages is well known and can be useful for various control release applications. DSC and TGA results indicate the presence of bound water closely interacting with the carbinol functional groups in the HPPS phase. This bound water could be removed at elevated temperatures above 140°C.

CHAPTER 6: CONCLUSIONS, MAIN ACCOMPLISHMENTS AND FUTURE WORK

6.1. CONCLUSIONS

The technology of formation of Interpenetrating Polymer Networks (IPNs) was successfully implemented for incorporation of biobased soybean oil triglycerides with polysiloxanes. Intimate mixing of these components with no gross phase separation was achieved by crosslinking the two immiscible components. These crosslinks were obtained by grafting reactive silanes onto the soybean oil that condense via silanol condensation to yield a network held together by siloxane linkages. The grafting process was optimized using Box – Behnken statistical experimental design. A semi-empirical model based on the Donatelli's equation was developed and successfully applied to the data to determine the crosslink density of these IPNs.

Different types of high molecular weight polysiloxanes were used in the preparation of these IPNs. One method consisted of emulsion polymerization whereby silanol terminated siloxanes oligomers were prepared. Here the IPN latex method was utilized. Alternatively, high molecular polysiloxanes were dissolved in a common solvent with the silylated soybean oil. In this case, a solvent-based IPN method was utilized.

A new class of hydrophilic polysiloxanes (HPPS) has been developed that are composed of pendant carbinol group on each repeat unit of the polysiloxane chain similar to polyvinyl alcohol. Unlike conventional water soluble silanes and other polar siloxanes, these HPPS are water soluble and the solubility is independent of the water pH. Completely solubility in water was attained even at high molecular weights. These types of polysiloxanes have not previously been disclosed and due to their surface properties and hydrophilicity, they may open new fields for siloxane applications. IPNs were successfully made and characterized using these HPPS polymers with silylated soybean oil and appeared to be useful in applications ranging from cosmetic, personal care products to environmentally degradable coatings.

6.2. MAIN ACCOMPLISHMENTS

The main achievement of this research work was the development of a new technology that enables the incorporation and crosslinking of biobased oils and siloxane into a series of new IPNs. Previously, the lack of specific interactions and the inherent incompatibility of biobased triglycerides with polysiloxanes prevented combining these materials together for any useful applications. Using the IPN approach allowed us to prepare new compositions from these immiscible components independent of their viscosities or molecular weights that exhibit no gross phase separation and interesting physical properties that are different from the properties of the individual components.

6.3. FUTURE RECOMMENDATIONS

All the IPNs developed were tested for coating applications on a hard surface such as wood or masonry. However, these IPNs can also be coated on softer substrates such as fabric. Initial data indicate that the coated fabrics tend to show better smoothness and improved "feel" of the material. The properties of these IPNs could be modified and the IPNs tested for such fabric coating applications.

Conventional siloxane polymers are widely used in the cosmetic and personal care industries. Since the combination of 'soft' polysiloxane and the consumer preference in personal care and cosmetics application is highly desirable, the experiments in this thesis can provide the basis for another area of potential applications. Controlling the ratio of the siloxane content to biobased content could be used to obtain useful materials for dermal and for hair care applications where hair smoothness and sebum control are desired.

The hydrophilic polysiloxanes developed could be copolymerized with different molecular weights of polydimethylsiloxanes to modify the surface properties of the copolymer. Having both hydrophilic as well as hydrophobic components, this could be designed for specific applications including new surfactants, amphiphobic coatings and stain resistant coatings. Modified surface properties of this polymer could also be explored in detachment lithography for nano-structures.

IPNs containing hydrolytically sensitive crosslinks could be explored further for applications as environmentally degradable coatings and controlled release applications. These IPNs are stable at neutral pH but completely degrade under other pH conditions. Thus, IPNs composed of these materials can be tailored to control the release rate of fertilizers or drugs to the environment and then completely degrade in the environment. REFERENCES

REFERENCES

- 1. Millar JR. Interpenetrating polymer networks. Styrene-Divinylbenzene Copolymers with Two and Three Interpenetrating Networks, and Their Sulphonates. Journal of the Chemical Society (Resumed) 1960:1311.
- 2. Sperling LH, Mishra V. The current status of interpenetrating polymer networks. Polymers for Advanced Technologies 1996:7(4):197-208.
- 3. Gupta N, Srivastava AK. INTERPENETRATING POLYMER NETWORKS A REVIEW ON SYNTHESIS AND PROPERTIES. Polymer International 1994:35(2):109-118.
- 4. Shi X, Graiver D, Narayan R. Hydrolysis and Condensation of Hydrophilic Alkoxysilanes Under Acidic Conditions. Silicon 2012:4(2):109-119.
- 5. Narayan R. Plastics from renewable resources. 2005. p. 391-397.
- 6. Narayan R. Rationale, drivers, standards and technology for biobased materials. Renewable resources and renewable energy—a global challenge 2006:1208863900.
- 7. Narayan R. Biobased and biodegradable polymer materials: rationale, drivers, and technology exemplars. 2006. p. 282.
- 8. Narayan R. Carbon footprint of bioplastics using biocarbon content analysis and life-cycle assessment. MRS bulletin 2011:36(09):716-721.
- 9. Biopreferred U. 2014.
- 10. Barrett LW, Sperling LH, Gilmer JW, Mylonakis SG. Semi-interpenetrating Polymer Networks Composed of Poly(ethylene terephthalate) and Castor Oil. American Chemical Society, 1994. p. 489-516.
- 11. Yenwo GM, Manson JA, Pulido J, Sperling LH, Conde A, Devia N. Castor-Oil-Based Interpenetrating Polymer Networks - Synthesis and Characterization. Journal of Applied Polymer Science 1977:21(6):1531-1541.
- 12. Devia N, Manson JA, Sperling LH, Conde A. Simultaneous Interpenetrating Networks Based on Castor Oil Elastomers and Polystyrene. 2. Synthesis and Systems Characteristics. Macromolecules 1979:12(3):360-369.
- 13. Patel M, Suthar B. Interpenetrating Polymer Networks from Castor-Oil Based Polyurethane and Poly(Methyl Methacrylate) .3. Angew Makromol Chem 1987:149:111-117.

- 14. Patel M, Suthar B. Interpenetrating Polymer Networks from Castor-Oil Based Polyurethanes and Poly(Methyl Acrylate) .4. European Polymer Journal 1987:23(5):399-402.
- 15. Patel M, Suthar B. Interpenetrating Polymer Networks from Castor-Oil Based Polyurethanes and Poly(Normal-Butyl Acrylate) .6. Int J Polym Mater 1987:12(1):43-52.
- 16. Suthar B, Dave M, Jadav K. Sequential-Interpenetrating Polymer Networks from Castor Oil-Based Polyesters .26. Journal of Applied Polymer Science 1993:50(12):2143-2147.
- 17. Barrett LW, Shaffer OL, Sperling LH. Semiinterpenetrating Polymer Networks Composed of Poly(Ethylene-Terephthalate) and Vernonia Oil. Journal of Applied Polymer Science 1993:48(6):953-968.
- 18. Linne MA, Sperling LH, Fernandez AM, Qureshi S, Manson JA. Simultaneous Interpenetrating Networks Prepared from Special Functional-Group Triglyceride Oils -Lesquerella-Palmeri and Other Wild Plant Oils. Adv Chem Ser 1984(208):37-49.
- 19. Sperling LI. Recent Developments in Interpenetrating Polymer Networks and Related Materials. 1985:211:21-56.
- 20. Sperling LH, Manson JA, Qureshi S, Fernandez AM. Tough plastics and reinforced elastomers from renewable resource industrial oils. A short review. Industrial & Engineering Chemistry Product Research and Development 1981:20(1):163-166.
- 21. Sperling LH, Manson JA, Jordhamo GM. Special Functional Triglyceride Oils as Reactive Oligomers for Simultaneous Interpenetrating Networks. 1985:282:237-249.
- 22. LinnÉ MA, Sperling LH, Fernandez AM, Qureshi S, Manson JA. Simultaneous Interpenetrating Networks Prepared from Special Functional Group Triglyceride Oils. 1984:208:37-49.
- 23. Sharma V, Kundu PP. Condensation polymers from natural oils. Prog Polym Sci 2008:33(12):1199-1215.
- 24. Ash M. USDA Economic Research Service-Market Outlook for Soybean Oil Crops. 2013.
- 25. Lucas P, Robin J-J. Silicone-Based Polymer Blends: An Overview of the Materials and Processes. 2007:209:111-147.
- 26. Turner JS, Cheng YL. Preparation of PDMS-PMAA interpenetrating polymer network membranes using the monomer immersion method. Macromolecules 2000:33(10):3714-3718.
- 27. Abbasi F, Mirzadeh H, Katbab AA. Comparison of viscoelastic properties of polydimethylsiloxane/poly(2-hydroxyethyl methacrylate) IPNs with their physical blends. Journal of Applied Polymer Science 2002:86(14):3480-3485.

- 28. Abbasi F, Mirzadeh H, Katbab AA. Sequential interpenetrating polymer networks of poly(2-hydroxyethyl methacrylate) and polydimethylsiloxane. Journal of Applied Polymer Science 2002:85(9):1825-1831.
- 29. Hron P, Slechtova J, Smetana K, Dvorankova B, Lopour P. Silicone rubber hydrogel composites as polymeric biomaterials .9. Composites containing powdery polyacrylamide hydrogel. Biomaterials 1997:18(15):1069-1073.
- Lednicky F, Janatova V, Lopour P, Vondracek P. Silicone Rubber-Hydrogel Composites as Polymeric Biomaterials .3. An Investigation of Phase Distribution by Scanning Electron-Microscopy. Biomaterials 1991:12(9):848-852.
- 31. Lopour P, Janatova V. Silicone Rubber-Hydrogel Composites as Polymeric Biomaterials .6. Transport-Properties in the Water-Swollen State. Biomaterials 1995:16(8):633-640.
- 32. Lopour P, Plichta Z, Volfova Z, Hron P, Vondracek P. Silicone-Rubber Hydrogel Composites as Polymeric Biomaterials .4. Silicone Matrix Hydrogel Filler Interaction and Mechanical-Properties. Biomaterials 1993:14(14):1051-1055.
- 33. Lopour P, Vondracek P, Janatova V, Sulc J, Vacik J. Silicone-Rubber Hydrogel Composites as Polymeric Biomaterials .2. Hydrophilicity and Permeability to Water-Soluble Low-Molecular-Weight Compounds. Biomaterials 1990:11(6):397-402.
- 34. Miyata T, Higuchi J, Okuno H, Uragami T. Preparation of polydimethylsiloxane/polystyrene interpenetrating polymer network membranes and permeation of aqueous ethanol solutions through the membranes by pervaporation. Journal of Applied Polymer Science 1996:61(8):1315-1324.
- 35. Garg P, Singh RP, Choudhary V. Selective polydimethylsiloxane/polyimide blended IPN pervaporation membrane for methanol/toluene azeotrope separation. Separation and Purification Technology 2011:76(3):407-418.
- 36. Jia L-Y, Zhang C, Du Z-J, Li C-J, Li H-Q. A novel approach to interpenetrating networks of epoxy resin and polydimethylsiloxane. Journal of Applied Polymer Science 2007:105(5):2663-2669.
- 37. Vuillequez A, Moreau J, Garda MR, Youssef B, Saiter JM. Polyurethane methacrylate/silicone interpenetrating polymer networks synthesis, thermal and mechanical properties. Journal of Polymer Research 2007:15(2):89-96.
- 38. Vlad S, Vlad A, Oprea S. Interpenetrating polymer networks based on polyurethane and polysiloxane. European Polymer Journal 2002:38(4):829-835.
- 39. Dobkowski Z, Zielecka M. Thermal analysis of the poly(siloxane)poly(tetrafluoroethylene) coating system. J Therm Anal Calorim 2002:68(1):147-158.

- 40. Murray DL, Hale WR, Jones AS. Nylon 6-Silicone Blends. In: Organization WP, editor. United States of America: Eastman Chemical Company, 2000. p. 24.
- 41. Barikani M, Hepburn C. Determination of Crosslink Density by Swelling in the Castable Polyurethane Elastomer Based on ¹/₄-Cyclohexane Diisocyanate and para-Phenylene Diisocyanate. Iranian J Polym Sci Tech 1992:1:1-5.
- 42. Omidian H, Hasherni S-A, Askari F, Nafisi S. Swelling and crosslink density measurements for hydrogels. Iranian J of Polymer Science and Technology Vol 1994:3(2).
- 43. Wood LA. Uniaxial Extension and Compression in Stress-Strain Relations of Rubber. Rubber Chem Technol 1978:51(4):840-851.
- 44. Sombatsompop N. Practical concerns regarding the use of the Mooney-Rivlin equation to assess degree of crosslinking of swollen rubber vulcanisates. Polymers & polymer composites 1999:7(1):41-44.
- 45. Flory PJ. Principles of polymer chemistry. Cornell University Press, 1953.
- 46. Meier DJ. Theory of block copolymers. I. Domain formation in A-B block copolymers. Wiley Online Library, 1969. p. 81-98.
- 47. Dewasthale S, Shi X, Hablot E, Graiver D, Narayan R. Interpenetrating polymer networks derived from silylated soybean oil and polydimethylsiloxane. Journal of Applied Polymer Science 2013:130(4):2479-2486.
- 48. Sperling L. Recent advances in interpenetrating polymer networks. Polymer Engineering & Science 1985:25(9):517-520.
- 49. Donatelli A, Sperling L, Thomas D. A semiempirical derivation of phase domain size in interpenetrating polymer networks. Journal of Applied Polymer Science 1977:21(5):1189-1197.
- 50. Michel J, Hargest S, Sperling L. Theoretical phase domain sizes in IPNs and related materials. Journal of Applied Polymer Science 1981:26(2):743-746.
- 51. Yeo J, Sperling L, Thomas D. Theoretical prediction of domain sizes in IPN's and related materials. Polymer 1983:24(3):307-313.
- 52. Shobha HK, Kishore K. Structural expressions of long-chain esters on their plasticizing behavior in poly(vinyl chloride). Macromolecules 1992:25(25):6765-6769.
- 53. Barrett LW, Sperling LH, Gilmer J, Mylonakis SG. Crystallization kinetics of poly(ethylene terephthalate) in compositions containing naturally functionalized triglyceride oil. Journal of Applied Polymer Science 1993:48(6):1035-1050.

- 54. Barrett L, Sperling L, Murphy C. Naturally functionalized triglyceride oils in interpenetrating polymer networks. Journal of the American Oil Chemists' Society 1993:70(5):523-534.
- 55. Sperling L H. Interpenetrating Polymer Networks and Related Materials. London: Plenum Press, 1981.
- 56. Devia N, Manson JA, Sperling LH, Conde A. Simultaneous Interpenetrating Networks Based on Castor-Oil Elastomers and Polystyrene .3. Morphology and Glass-Transition Behavior. Polym Eng Sci 1979:19(12):869-877.
- 57. Athawale V, Raut S. New interpenetrating polymer networks based on uralkyd/poly(glycidyl methacrylate). European Polymer Journal 2002:38:2033-2040.
- 58. Raut S, Athawale V. New elastomers based on uralkyd/polyethyl methacrylate semi- and full interpenetrating polymer networks. J Polym Sci Pol Chem 1999:37(23):4302-4308.
- 59. Athawale V, Raut S. New interpenetrating polymer networks based on uralkyd–poly(butyl methacrylate). Polymer International 2001:50:1234-1240.
- 60. Barrett LW, Shaffer OL, Sperling LH. Semi-interpenetrating polymer networks composed of poly(ethylene terephthalate) and vernonia oil. Journal of Applied Polymer Science 1993:48(6):953-968.
- 61. Fernandez AM, Manson JA, Sperling L H. Renewable Resources Materials: New Polymer Sources. New York: Plenum Press, 1986.
- 62. Afolabi OA, Aluko ME, Wang GC, Anderson WA, Ayorinde FO. Synthesis of Toughened Elastomer from Vernonia-Galamensis Seed Oil. J Am Oil Chem Soc 1989:66(7):983-985.
- 63. Linne MA, Sperling LH, Fernandez AM, Qureshi S, Manson JA. Simultaneous Interpenetrating Networks Prepared from Special Functional-Group Triglyceride Oils -Lesquerella Palmeri and Other Wild Plant Oils. Abstr Pap Am Chem S 1983:186(Aug):114-PMSE.
- 64. Zhou P, Frisch HL, Rogovina L, Makarova L, Zhdanov A, Sergeienko N. Interpenetrating polymer networks of poly(dimethyl siloxane–urethane) and poly(methyl methacrylate). Journal of Polymer Science Part A: Polymer Chemistry 1993:31(10):2481-2491.
- 65. Gilmer TC, Hall PK, Ehrenfeld H, Wilson K, Bivens T, Clay D, Endreszl C. Synthesis, characterization, and mechanical properties of PMMA/poly(aromatic/aliphatic siloxane) semi-interpenetrating polymer networks. Journal of Polymer Science Part A: Polymer Chemistry 1996:34(6):1025-1037.

- 66. Chang TC, Wu KH, Liao CL, Wang GP. Characterization and degradation of poly(methylphenylsiloxane)–poly(methyl methacrylate) interpenetrating polymer networks. Journal of Polymer Science Part A: Polymer Chemistry 1999:37(11):1717-1724.
- 67. Erbil C, Kazancıoğlu E, Uyanık N. Synthesis, characterization and thermoreversible behaviours of poly(dimethyl siloxane)/poly(N-isopropyl acrylamide) semi-interpenetrating networks. European Polymer Journal 2004:40(6):1145-1154.
- 68. Hatada K, Kitayama T, Vogl O. Macromolecular Design of Polymeric Materials. New York: Marcel Dekker Inc., 1997.
- 69. Sperling LH, Sarge HD. Joined and sequential interpenetrating polymer networks based on poly(dimethylsiloxane). Journal of Applied Polymer Science 1972:16(11):3041-3046.
- 70. Sperling L H, Hu R. Interpenetrating Polymer Networks. Netherlands: Kluwer Academic Publishers, 2003.
- ASTM Standard D2765-11, Standard Test Methods for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene Plastics. West Conshohocken, PA: ASTM International, 2003, DOI 10.1520/C0033-03, <u>www.astm.org</u>.
- 72. ASTM Standard D638-10, Standard Test Method for Tensile Properties of Plastics. West Conshohocken, PA: ASTM International, 2003, DOI: 10.1520/C0033-03, <u>www.astm.org</u>.
- 73. Graiver D, Huebner DJ, Saam JC. Emulsion Polymerized Polydimethylsiloxane. Rubber Chem Technol 1983:56(5):918-926.
- 74. Saam JC, Graiver D, Baile M. Room-Temperature-Cured Polydimethylsiloxane Elastomers from Aqueous Dispersion. Rubber Chem Technol 1981:54(5):976-987.
- 75. Chojnowski J, Cypryk M. Synthesis of Linear Polysiloxanes. In: Jones R, Ando W, Chojnowski J, editors: Springer Netherlands, 2000. p. 3-41.
- 76. Graiver D, Saam JC, Baile M. Network Development in Films Cast from Emulsions of Polydimethylsiloxane. Abstr Pap Am Chem S 1981:181(Mar):38-ORPL.
- 77. Wu Y, Chen Z, Zeng X. Nanoscale morphology for high hydrophobicity of a hard sol–gel thin film. Appl Surf Sci 2008:254(21):6952-6958.
- 78. Speier JL, Webster JA, Barnes GH. The Addition of Silicon Hydrides to Olefinic Double Bonds. Part II. The Use of Group VIII Metal Catalysts. Journal of the American Chemical Society 1957:79(4):974-979.
- Fink M. Comprehensive Handbook on Hydrosilylation. Herausgegeben von B. Marciniec. Pergamon Press, Oxford, 1992. 754 S., geb. 150.00 £. – ISBN 0-08-040272-0. Angewandte Chemie 1995:107(1):131-132.

- Ojima I, Li Z, Zhu J. Recent Advances in the Hydrosilylation and Related Reactions. John Wiley & Sons, Ltd, 2009.
- 81. Motokura K, Baba T. An atom-efficient synthetic method: carbosilylations of alkenes, alkynes, and cyclic acetals using Lewis and Bronsted acid catalysts. Green Chemistry 2012:14(3):565-579.
- 82. Asao N, Yamamoto Y. Lewis Acid-Catalyzed Hydrometalation and Carbometalation of Unactivated Alkynes. Bulletin of the Chemical Society of Japan 2000:73(5):1071-1087.
- 83. Jung IN, Yoo BR. Lewis Acid-Catalyzed Regio- and Stereoselective Allylsilation of Simple Unsaturated Hydrocarbons. Synlett 1999:1999(05):519-528.
- 84. Song Y-S, Yoo BR, Lee G-H, Jung IN. Lewis acid-catalyzed regio-and stereoselective hydrosilylation of alkenes with trialkylsilanes. Organometallics 1999:18(16):3109-3115.
- 85. Wakatsuki Y, Yamazaki H, Nakano M, Yamamoto Y. Ruthenium-catalysed disproportionation between vinylsilanes and mono-substituted alkenes via silyl group transfer. J Chem Soc, Chem Commun 1991(10):703-704.
- 86. Pawluć P, Prukała W, Marciniec B. Silylative Coupling of Olefins with Vinylsilanes in the Synthesis of π -Conjugated Double Bond Systems. European Journal of Organic Chemistry 2010:2010(2):219-229.
- 87. Marciniec B. Catalytic Coupling of sp2- and sp-Hybridized Carbon–Hydrogen Bonds with Vinylmetalloid Compounds. Accounts of Chemical Research 2007:40(10):943-952.
- 88. Marciniec B. Catalysis by transition metal complexes of alkene silylation–recent progress and mechanistic implications. Coordination chemistry reviews 2005:249(21):2374-2390.
- 89. Alder K, Pascher F, Schmitz A. Über die Anlagerung von Maleinsäure-anhydrid und Azodicarbonsäure-ester an einfach ungesättigte Koh an einfach ungesättigte Kohlenwasserstoffe. Zur Kenntnis von Substitutionsvorgängen in der Allyl-Stellung. Berichte der deutschen chemischen Gesellschaft (A and B Series) 1943:76(1-2):27-53.
- 90. Mikami K, Loh TP, Nakai T. Carbonyl-ene reaction with vinylsilanes: silicon as a controlling element for regio-and stereochemistry. Journal of the American Chemical Society 1990:112(18):6737-6738.
- 91. Zhao F, Zhang S, Xi Z. Silyl-substituted 1, 3-butadienes for Diels–Alder reaction, ene reaction and allylation reaction. Chemical Communications 2011:47(15):4348-4357.
- 92. Srinivasan M. Synthesis, properties and applications of bio-based materials. Ann Arbor: Michigan State University, 2010. p. 272.

- 93. Zhuang Y. Novel synthetic route to biobased silylated soybean oil for use as coating material. United States -- Michigan: Michigan State University, 2011.
- 94. Thompson KE. Design and engineering of bio-based coating for use on paper and other substrates. Ann Arbor: Michigan State University, 2013. p. 109.
- 95. Dubac J, Laporterie A. Ene and Retro-Ene Reactions in Group 14 Organometallic Chemistry. Chemistry Review 1987:87:319-334.
- 96. Weyenberg DR, Mahone LG, Atwell WH. REDISTRIBUTION REACTIONS IN THE CHEMISTRY OF SILICON. Annals of the New York Academy of Sciences 1969:159(1):38-55.
- 97. Peppard DF, Brown WG, Johnson WC. Preparation and Synthetic Applications of Alkyl Chlorosilicates. Journal of the American Chemical Society 1946:68(1):70-72.
- 98. Brinker C. Hydrolysis and condensation of silicates: effects on structure. Journal of Non-Crystalline Solids 1988:100(1):31-50.
- 99. Narayan R. Principles, Drivers, and Analysis of Biodegradable and Biobased Plastics. Rapra Technology, 2014. p. 561-582.
- 100. Iler RK. Chemistry of Silica. New York: John Wiley & Sons, 1979.
- 101. Donatelli A, Sperling L, Thomas D. Interpenetrating polymer networks based on SBR/PS.
 1. Control of morphology by level of cross-linking. Macromolecules 1976:9(4):671-675.
- 102. Siegfried D, Manson J, Sperling L. Viscoelastic behavior and phase domain formation in Millar interpenetrating polymer networks of polystyrene. Journal of Polymer Science: Polymer Physics Edition 1978:16(4):583-597.
- 103. Hargest S, Manson J, Sperling L. Characterization of anionic/cationic sequential IPNs. II. Studies of swelling, modulus, and alternate phase staining with CsF and LiI. Journal of Applied Polymer Science 1980:25(3):469-485.
- 104. Yenwo G, Sperling L, Manson J, Conde A, Labana S. Chemistry and Properties of Crosslinked Polymers. Labana, SS, Ed 1977:257.
- 105. Sumi D, Dhanabalan A, Thimmappa BHS, Krishnamurthy S. Effect of colloidal silica dispersions on the properties of PDMS-colloidal silica composites. Journal of Applied Polymer Science 2012:125(S1):E515-E522.
- 106. Koerner G. Silicones, Chemistry and Technology. CRC Press, 1992.
- 107. Narayan R. Biobased and biodegradable materials: drivers, rationale and technology exemplars. 2006.

- 108. Klempner D, Frisch KC, Frisch HL. Nomenclature of Interpenetrating Polymer Networks. Journal of Elastomers and Plastics 1973:5(4):196-200.
- 109. Mello VM, Oliveira GV, Suarez PAZ. Turning Used Frying Oil into a New Raw Material to Printing Inks. Journal of the Brazilian Chemical Society 2013:24(2):314-319.
- Erhan SZ, Sharma BK, Liu Z, Adhvaryu A. Lubricant Base Stock Potential of Chemically Modified Vegetable Oils. Journal of Agricultural and Food Chemistry 2008:56(19):8919-8925.
- Lathi P, Mattiasson B. Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil. Applied Catalysis B: Environmental 2007:69(3-4):207-212.
- 112. Biswas A, Adhvaryu A, Stevenson DG, Sharma BK, Willet JL, Erhan SZ. Microwave irradiation effects on the structure, viscosity, thermal properties and lubricity of soybean oil. Industrial Crops and Products 2007:25(1):1-7.
- 113. Zhao X, Yang J, Tao D, Xu X. Synthesis and Tribological Properties of Air Plasma Polymerized Soybean Oil with N-Containing Structures. Journal of the American Oil Chemists' Society 2014:91(5):827-837.
- 114. Erhan SZ, Bagby MO. Polymerization of vegetable oils and their uses in printing inks. Journal of the American Oil Chemists' Society 1994:71(11):1223-1226.
- 115. Lozada Z, Suppes GJ, Hsieh F-H, Lubguban A, Tu Y-C. Preparation of polymerized soybean oil and soy-based polyols. Journal of Applied Polymer Science 2009:112(4):2127-2135.
- 116. Adams HE, Powers PO. Thermal Polymerization of Drying Oils. Journal of Applied Physics 1946:17(5):325-337.
- 117. Gupta N, Srivastava A. Interpenetrating polymer networks: a review on synthesis and properties. Polymer international 1994:35(2):109-118.
- 118. Bajpai AK, Bajpai J, Shukla S. Water sorption through a semi-interpenetrating polymer network (IPN) with hydrophilic and hydrophobic chains. Reactive and Functional Polymers 2002:50(1):9-21.
- 119. Thanoo BC, Sunny MC, Jayakrishnan A. Controlled Release of Oral Drugs from Crosslinked Polyvinyl Alcohol Microspheres. Journal of Pharmacy and Pharmacology 1993:45(1):16-20.
- 120. Carstensen JT, Marty J-P, Puisieux F, Fessi, Hatem. Bonding mechanisms and hysteresis areas in compression cycle plots. Journal of Pharmaceutical Sciences 1981:70(2):222-223.
- 121. Yao KD, Peng T, Feng HB, He YY. Swelling kinetics and release characteristic of crosslinked chitosan: Polyether polymer network (semi-IPN) hydrogels. Journal of Polymer Science Part A: Polymer Chemistry 1994:32(7):1213-1223.
- 122. Wang H, Li W, Lu Y, Wang Z. Studies on chitosan and poly (acrylic acid) interpolymer complex. I. Preparation, structure, pH-sensitivity, and salt sensitivity of complex-forming poly (acrylic acid): Chitosan semi-interpenetrating polymer network. Journal of applied polymer science 1997:65(8):1445-1450.
- 123. Lee JW, Kim SY, Kim SS, Lee YM, Lee KH, Kim SJ. Synthesis and characteristics of interpenetrating polymer network hydrogel composed of chitosan and poly (acrylic acid). Journal of Applied Polymer Science 1999:73(1):113-120.
- 124. Zhang J, Peppas NA. Synthesis and characterization of pH-and temperature-sensitive poly (methacrylic acid)/poly (N-isopropylacrylamide) interpenetrating polymeric networks. Macromolecules 2000:33(1):102-107.
- 125. Langer R, Peppas N. Chemical and physical structure of polymers as carriers for controlled release of bioactive agents: a review. Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics 1983:23(1):61-126.
- 126. Folkman J, Winsey S, Moghul T. New Approach to Analgesia and Anesthesia Anesthesia by Diffusion through Silicone Rubber. Anesthesiology 1968:29(3):410-418.
- 127. Gaginella TS, Welling PG, Bass P. Nicotine base permeation through silicone elastomers: Comparison of dimethylpolysiloxane and trifluoropropylmethylpolysiloxane systems. Journal of Pharmaceutical Sciences 1974:63(12):1849-1853.
- 128. Olanoff L, Anderson J, Jones R. Sustained release of gentamicin from prosthetic heart valves. ASAIO Journal 1979:25(1):334-338.
- 129. Dziuk P, Cook B. Passage of steroids through silicone rubber. Endocrinology 1966:78(1):208-211.
- 130. Shaviv A. Advances in controlled-release fertilizers. Advances in agronomy 2001:71:1-49.
- 131. Trenkel ME, Association IFI. Controlled-release and stabilized fertilizers in agriculture. International Fertilizer Industry Association Paris, 1997.
- 132. Zhang X, Lin G, Kumar SR, Mark JE. Hydrogels prepared from polysiloxane chains by end linking them with trifunctional silanes containing hydrophilic groups. Polymer 2009:50(23):5414-5421.
- 133. Barbier V, Tatoulian M, Li H, Arefi-Khonsari F, Ajdari A, Tabeling P. Stable modification of PDMS surface properties by plasma polymerization: application to the formation of double emulsions in microfluidic systems. Langmuir 2006:22(12):5230-5232.

- 134. Makamba H, Kim JH, Lim K, Park N, Hahn JH. Surface modification of poly (dimethylsiloxane) microchannels. Electrophoresis 2003:24(21):3607-3619.
- 135. Trimbach DC, Al-Hussein M, de Jeu WH, Decré M, Broer DJ, Bastiaansen CW. Hydrophilic elastomers for microcontact printing of polar inks. Langmuir 2004:20(11):4738-4742.
- 136. Wang R, Yang Y-L, Qin M, Wang L-K, Yu L, Shao B, Qiao M-Q, Wang C, Feng X-Z. Biocompatible hydrophilic modifications of poly (dimethylsiloxane) using self-assembled hydrophobins. Chemistry of materials 2007:19(13):3227-3231.
- 137. Gao Z, Schulze Nahrup J, Mark JE, Sakr A. Poly (dimethylsiloxane) coatings for controlled drug release. II. Mechanism of the crosslinking reaction in emulsion. Journal of applied polymer science 2004:91(4):2186-2194.
- 138. Gao Z, Nahrup JS, Mark JE, Sakr A. Poly (dimethylsiloxane) coatings for controlled drug release. III. Drug release profiles and swelling properties of the free-standing films. Journal of applied polymer science 2005:96(2):494-501.
- 139. Mashak A, Rahimi A. Silicone polymers in controlled drug delivery systems: a review. Iran Polym J 2009:18(4):279-295.
- 140. Roman GT, Culbertson CT. Surface engineering of poly (dimethylsiloxane) microfluidic devices using transition metal sol-gel chemistry. Langmuir 2006:22(9):4445-4451.
- 141. Hong SM, Kim SH, Kim JH, Hwang HI. Hydrophilic surface modification of PDMS using atmospheric RF plasma. IOP Publishing, 2006. p. 656.
- 142. Efimenko K, Wallace WE, Genzer J. Surface modification of Sylgard-184 poly (dimethyl siloxane) networks by ultraviolet and ultraviolet/ozone treatment. Journal of Colloid and Interface Science 2002:254(2):306-315.
- 143. Gongjian B, Yunxuan W, Xingzhou H. Surface modification of polyolefine by UV light/ozone treatment. Journal of applied polymer science 1996:60(13):2397-2402.
- 144. Hillborg H, Gedde U. Hydrophobicity recovery of polydimethylsiloxane after exposure to corona discharges. Polymer 1998:39(10):1991-1998.
- 145. Lee CF, Hsieh PH, Ghosh SK, Kuo PL. Emulsifying and self-emulsified properties of siloxane polymer grafted with easy hydrophile. Journal of applied polymer science 2002:86(10):2408-2415.
- 146. Hou S-S, Chung Y-P, Chan C-K, Kuo P-L. Function and performance of silicone copolymer. Part IV. Curing behavior and characterization of epoxy–siloxane copolymers blended with diglycidyl ether of bisphenol-A. Polymer 2000:41(9):3263-3272.

- 147. Hill RM. Silicone Surfactants. New York: Marcel Dekker, 1999.
- 148. Alexandru M, Cazacu M, Racles C, Grigoras C. Amphiphile polydimethylsiloxane-based networks reinforced with in situ generated silica. Polymer Engineering & Science 2011:51(1):78-86.
- 149. Cazacu M, Ioanid A, Ioanid G, Racles C, Vlad A. Amphiphilic sorbents based on polysiloxanes crosslinked by an N, N'-heterocycle. Applied organometallic chemistry 2006:20(8):494-498.
- 150. Iwakiri N, Nishikawa T, Kaneko Y, Kadokawa J-I. Synthesis of amphiphilic polysiloxanes and their properties for formation of nano-aggregates. Colloid and Polymer Science 2009:287(5):577-582.
- 151. Kaneko Y, Iyi N, Kurashima K, Matsumoto T, Fujita T, Kitamura K. Hexagonal-structured polysiloxane material prepared by sol-gel reaction of aminoalkyltrialkoxysilane without using surfactants. Chemistry of materials 2004:16(18):3417-3423.
- 152. Kaneko Y, Kadokawa J-i, Setoguchi M, Iyi N. Synthesis of rodlike polysiloxane containing polyol moieties derived from glucose with regularly controlled higher-ordered structure. Polymer 2005:46(21):8905-8907.
- 153. Tachibana Y, Shi X, Graiver D, Narayan R. Hydroxyl Terminated Hydrophilic Silanes. Silicon 2012:4(3):167-174.
- 154. Launer PJ. Infrared analysis of organosilicon compounds: spectra-structure correlations. Silicone Compounds Register and Review 1987:100-103.
- 155. Jayasekara R, Harding I, Bowater I, Christie G, Lonergan G. Preparation, surface modification and characterisation of solution cast starch PVA blended films. Polymer testing 2004:23(1):17-27.
- 156. Hassan CM, Peppas NA. Structure and applications of poly (vinyl alcohol) hydrogels produced by conventional crosslinking or by freezing/thawing methods. Springer, 2000. p. 37-65.
- 157. Goswami BC, Anandjiwala RD, Hall D. Textile Sizing. New York: Marcel Dekker, 2004.
- 158. Hassan CM, Peppas NA. Structure and Morphology of Freeze/Thawed PVA Hydrogels. Macromolecules 2000:33(7):2472-2479.
- 159. Holland B, Hay J. The thermal degradation of poly (vinyl alcohol). Polymer 2001:42(16):6775-6783.
- 160. Guirguis OW, Moselhey MT. Thermal and structural studies of poly (vinyl alcohol) and hydroxypropyl cellulose blends. Natural Science 2011:4(1):11.

- 161. Macan J, Ivanković H. Influence of Hydrolysis Conditions on Curing and Properties of an Epoxy-Silane Based Hybrid Material. 2006. p. 22-24.
- 162. Voronkov MG, Mileshkevich VP, Yuzhelevskii YA. The siloxane bond. Consultants Bureau, New York 1978:196.
- 163. Aelion R, Loebel A, Eirich F. Hydrolysis of Ethyl Silicate*. J Am Chem Soc 1950:72(12):5705-5712.
- 164. Keefer K, Brinker CJ, Clark D, Ulrich D. Better ceramics through chemistry. 1984. p. 15.
- 165. Graiver D, Farminer KW, Narayan R. A Review of the Fate and Effects of Silicones in the Environment. Journal of Polymers and the Environment 2003:11(4):129-136.