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PROCESSING PARAMETER - PROPERTY RELATIONS OF
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presented by

LALITA HARISH WAIKUL

has been accepted towards fulfillment
of the requirements for

M.S. degree in CHEMICAL ENGINEERING

Ramani Narayan
Major professor

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PROCESSING PARAMETER - PROPERTY RELATIONS OF SOY PROTEIN - COPOLYESTER BLENDS

By

Lalita Harish Waikul

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

DEPARTMENT OF CHEMICAL ENGINEERING

1998

ABSTRACT

PROCESSING PARAMETER - PROPERTY RELATIONS OF SOY PROTEIN - COPOLYESTER BLENDS

By

Lalita Harish Waikul

A study of the effect of various process parameters on the properties Eastar Bio Copolyester blended with soy protein was conducted. Extrusion was the primary process used for all mixing purposes. Injection molding was used to prepare tensile test samples. The materials synthesized were characterized for mechanical properties, namely - tensile strength and percent elongation. Differential scanning calorimetry was used to obtain information on melting point depression to check for miscibility. Scanning electron microscopy of fractured tensile specimens was used to study morphology. Some of the critical process parameters varied were composition, screw configuration and thermal history. Film formability was also verified using a cast film technique. An improvement in mechanical properties was achieved by suitably varying the process parameters and introducing a plasticizer.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Ramani Narayan for his guidance and support. Many people in the Department of Chemical Engineering, Composite Materials and Structures Center and Michigan Biotechnology Institute have helped me during my work, in so many different ways. It is hard to name everyone individually without missing someone. I would like to thank them all. Special thanks to my colleagues Tina Kiley, Megan Rich and Dale Smith.

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ABBREVIATIONS

EPE	Eastar bio copolyester
SF	Soy flour
SC	Soy concentrate
SI	Soy isolate
GLY	Glycerol
EG	Ethylene glycol
PSC(EG)	Soy concentrate plasticized with ethylene glycol in weight ratio 70:30
PSC(G)or PSC(GLY)	Soy concentrate plasticized with glycerol in weight ratio 70:30
PSC	Soy concentrate plasticized with glycerol in an extruder when no other details are indicated
CMP PSC	SC plasticized first by simple mechanical mixing and then in an extruder
UNCMP PSC	SC plasticized in only by simple mechanical mixing and not in an extruder
A:B::X:Y	X lbs. of A blended with Y lbs. of B
ESEM	Environmental Scanning Electron Microscopy
DSC	Differential Scanning Calorimetry
TGA	Thermo-Gravimetric Analysis
Tm	Melting point temperature
Tg	Glass transistion temperature

Tc	Annealing temperature or crystallization temperature
*	Guage length during tensile testing was reduced to 2″
**	Sample did could not be tested to failure due elongation reaching jaw separation limits.
D638	ASTM standard for mechanical testing of polymers
D882	ASTM standard for mechanical testing of polymer films
EXC	Extruded at X degrees C
IYC	Injection molded at Y degrees C

1. INTRODUCTION

Many agricultural materials contain proteins, which are essentially macromolecules. Hence the idea of exploiting these natural resources to make plastic articles has been around for a while. The primary reasons for trying to make plastics from renewable resources are (Narayan, 1991):

- Biodegradability of plastics as a means for environment-friendly disposal.
- An alternative to depleting non-renewable imported petroleum feedstock.
- Abundance of agricultural feedstock that could benefit from development of value added products.

Soy proteins, which are essentially polyamides obtained from soybeans, satisfy all the above criteria. Soy proteins and their derivatives can therefore be considered for partial or complete replacements for synthetic polymers.

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2. LITERATURE REVIEW

Mechanical properties and water absorption studies of plastics made by compression molding of cross-linked (Jane, 1997) and plasticized soy isolates (Jane, 1996) have been reported.

Cross-linking resulted in materials having mechanical properties comparable to engineering plastics with tensile modulli of 4.4Gpa, much higher than commonly utilized petrochemical engineering plastics (Epoxy - 3.00GPa, Polycarbonate - 2.1GPa). Plastics made from soy protein alone were very rigid and brittle. Moreover, the data reported were based on use of compression molding, which is not suitable for large volume production or for the manufacture of complex shape articles. A severe problem in the form of an order magnitude drop in the modulus was reported in presence of moisture at room temperature.

Plasticization with glycerol resulted in improved flexibility and an increase in percentage elongation at break. Tensile strengths of about 9MPa and a maximum %elongation at break of about 200% were attained using very high levels of plasticizer and using a plasticorder at very

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low rpms. Water absorption problems persisted. Most data reported were based on soy isolate, which is one of the more expensive sources of soy protein. Using other plasticizers like ethylene glycol as a plasticizer gave slightly higher percent elongation compared to use of glycerol. A lowering of the glass transition temperature from 150C to -50C on plasticization of soy isolate is reported based on dynamic mechanical spectroscopy. This lowering of the glass transition temperature induces thermoplastic behavior which makes it possible to melt soy protein before degradation commences (Jane, 1996).

The other important concern that has been identified and somewhat addressed is the drastic reduction of stiffness in moist environments as compared to synthetic polymers. Silane coupled polyphosphate fillers were used to improve water resistance (Otaigbe, 1998). The work was again based on usage of compression molding and does not report the effect on mechanical properties.

There is considerable lack of information concerning the reactions between polyamide-polyester. Utracki's studies (Utracki and Pillion, 1984) on melt rheology of blends of PET and PA indicates a degree of association and/or co-crystallization involving the two polymers. Kamal has also reported a degree of compatibility in the molten state. Patent literature reveals that blending of PET/PA in the melt produces polyester-polyamide block polymers. Utracki and Pillion have used p-tolunesulphonic acid as a catalyst to achieve reaction between polyamides and polyesters requiring 2-4 minutes residence time. Most reactions tried by others (Firestone Tire & Rubber Co., 1969 and Toyo Rayon, 1969) even with catalyst required very long reaction times unsuitable for continuous processing

Polyamides are strongly polar polymers while polyesters are neutral polymers. Thus they are not theoretically miscible from a thermodynamic point of view. But this is hardly a deterrent, since adequate compatabilization through use of compatibilizers and appropriate processing conditions is a method commonly used in the plastics industry to effect property improvement in a number of commercially successful blends.

An extensive review by Kinsella (Kinsella, 1979) on the functional properties of soy proteins emphasizes the heterogeneity of soy proteins and gives details about the structural changes that occur under different temperatures

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and chemical conditions. On heating, soy proteins undergo denaturing, which involves permanent unfolding of soy protein structure and eventually degrade above 140C. Presence of thiols, sodium sulphite causes cleavage of intermolecular disulphide bonds increasing solubility. Soy proteins have an isoelectric point of 4.5

The mechanical properties of cast film depend on the amount of orientation that can be applied and retained in the polymer film. An optimum melt temperature and chill roll temperature is necessary so that the melt strength is adequate to sustain the orientation stresses. Annealing may also be necessary to prevent loss of orientation in use (Park W. R. R., 1969 and Park H. C., 1990)

THE PROBLEM:

The main block to commercialization of soy based plastics is - attempts made heretofore have all solved only a particular aspect of the problem either processability or water absorption or mechanical properties.

The problem can now be defined as the need for an integrated engineering solution to address simultaneously all individual aspects of the problem, namely -

processability, mechanical properties and water solubility in a single solution, with a keen eye on economics.

PROBLEM SOLVING APPROACH

The present work seeks to address the problem of processability, mechanical properties and moisture sensitivity in a single system. The properties and hence end use of any new plastic is inseparably linked with the choice of processing techniques and processing parameters. Hence property optimization involves optimal selection of materials, processing techniques and processing conditions.

Process equipment selection: Use of conventional processing equipment such as extruders is advocated to reduce cost of design from scratch and custom-built process equipment. The wide availability of this equipment also allows ease of installation of the process at any custom compounder's facility. Considering all above arguments, it was decided that all-experimental data be obtained using a labscale extruder. Another advantage of this choice is the ease of scaling (Bisio and Kabel, 1985).

Material selection: Traditional techniques like extrusion, injection molding, etc., require that materials to be processed be thermoplastic. Soy protein by itself in its natural form does not possess this property. On heating, soy protein undergoes permanent structural changes, called denaturing. Fortunately, thermoplasticity can be induced through additives like plasticizers or by blending with a thermoplastic having good processability and reasonable mechanical properties. Since plasticization by itself has been tried and did not prove adequate, this thesis explores the possibility of using blending. The idea of blending of two or more polymers to obtain an acceptable combination of properties is a common method in the plastics industry. Additionally most synthetic thermoplastics have very good barrier properties, which can reduce the vulnerability of the blends to moist environments. Using a biodegradable thermoplastic can also aid in retaining the inherent biodegradability and future value of the soy protein product.

Eastar bio copolyester 14766, a new film forming biodegradable polymer that was recently introduced by Eastman was found to satisfy all of the above criteria. It is intended to replace widely used non-biodegradable polyethylene films in disposable applications. Coupling of soy protein with this copolyester can lead to enormous e

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value addition to abundantly available soy proteins. Copolyester films had 19MPa tensile strength, high percent elongations and low viscosity above the melting point. The other popular biodegradable polymer, PCL was excluded due to its lower melting point (Tm PCL = 60C, Tm EPE = 112C) making products susceptible to deformation during storage and transportation.

The objective of this thesis can now be restated. It is to take a step towards the identification of optimal process design and parameters for blending of soy protein and EPE to obtain either an improvement or an acceptable reduction in mechanical properties, using traditional processing technique such as extrusion and injection molding.

To achieve this objective, a set of experiments was designed to observe the effect of varying composition and a set of important process parameters on the commercially important mechanical properties. Also, morphology and melting point behavior were studied to aid the fundamental understanding of the underlying phenomena (Figure 1).

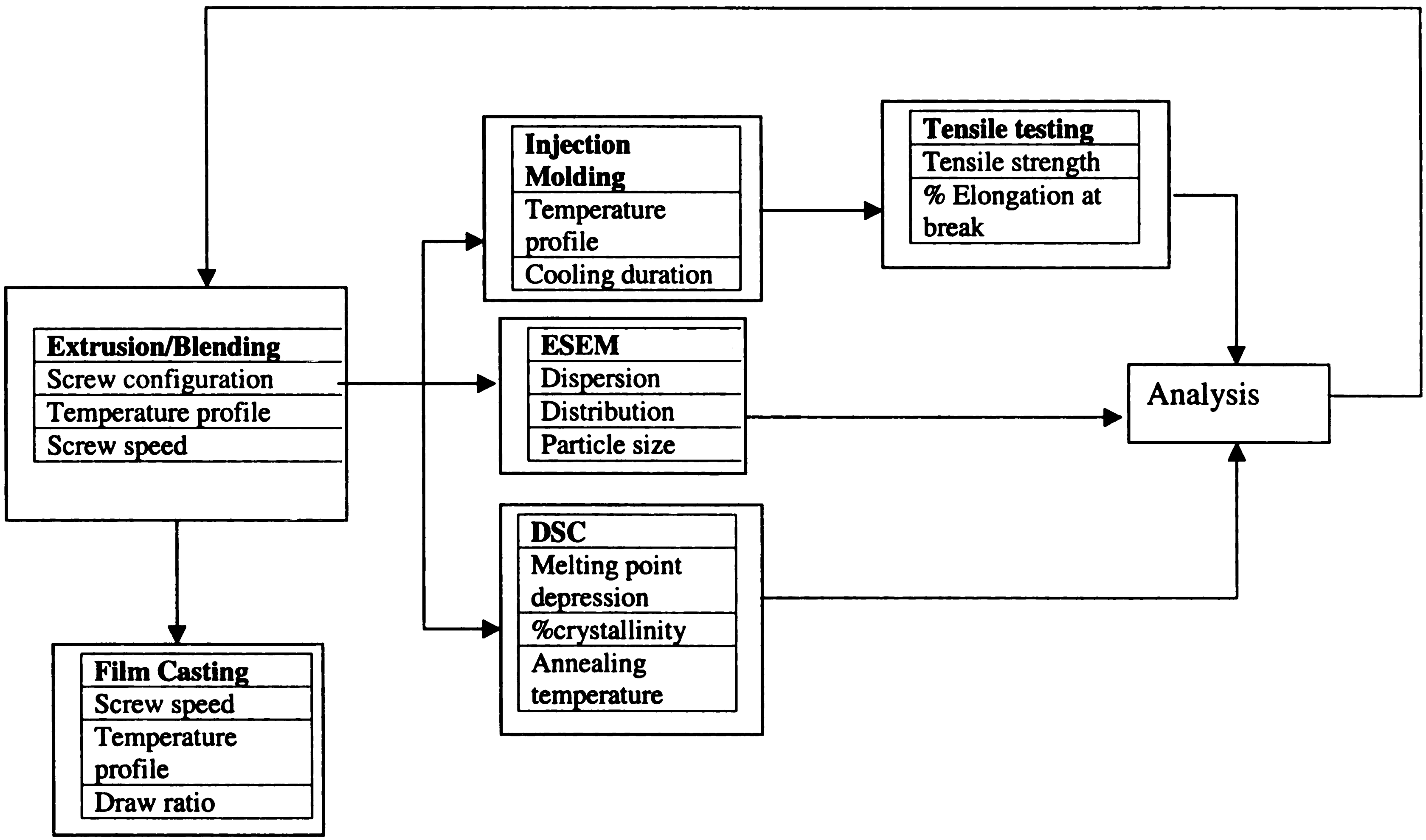

Figure 1 - Problem Solving Approach

3. RAW MATERIALS

3.A SOY-PROTEIN

Soy protein is available in three different forms - soy flour, soy concentrate and soy isolate. The lower the protein content, lower the cost. In order to maintain cost effectiveness of the end product only soy flour (SF) and soy concentrate(SC) were used.

TABLE 1 - SOY PROTEIN SOURCES

Protein source	**Cost $/IB**	**%protein**
Soy flour	0.15	52
Soy concentrate	0.77	65
Soy isolate	1.5	90

3.A.1 SOYFLOUR

Soyafluff 200W from Central Soya was used. It had a particle size (U.S. standard sieve) of 90Min% through #200. Soyflour is classified as per the heat treatment. The most soluble form of soy protein has the highest polydispersity index.

3.A.2 SOY-CONCENTRATE

Procon 2000 was obtained from Central Soya. Soy concentrates are classified depending on pH used to precipitate it. Procon 2000 had a pH of 4.5. It was selected because the acidic pH would be conducive to its interaction with glycerol. It also had a higher degradation temperature than Promax70. It had a particle size (U.S. Standard Sieve) 94Min% through #100 and a maximum moisture content of 10%.

3.B EASTMAN COPOLYESTER 14766

A new biodegradable polymer EASTAR BIO Copolyester (EPE) introduced by Eastman was used. It is a random copolyester of adipic acid, terephthalic acid and 1,4-butanediol (Buchanan, 1995).

TABLE 2 - EPE PROPERTIES

Melting point	112C
Glass transistion temperature	-33C
Mn	20 Kg/mole
Mw	67Kg/mole
M.W.D.	3.3
Theoretical heat of fusion for a 100% crystalline copolyester	91.96J/gm
Film tensile strength of 2 mil film(D882)	19Mpa
Max %elongation at break of 2 mil film(D882)	600%
Density	1.27 g/cm3
Cost of EPE	$2.15/Ib

4 PROCESSING TECHNIQUES

TGA degradation studies of all basic raw materials were carried out to determine limits on processing temperature conditions. EPE underwent a sharp weight loss at 350C and procon2000 above 180C.

Though the weight loss of soy protein powders commences after 180C, the reported degradation of soy-protein molecules starts at 140C suggesting an upper limit on extrusion temperatures. The melting point of the EPE at 112C set the lower limit. High temperatures are desirable to ensure flow-ability of EPE and hence good mixing.

4.A. SYNTHESIS

Mixing was done using a co-rotating twin screw extruder, ZSK-30, from Werner & Plfeiderer. All materials in pellet form were metered using a gravimetric acrison feeder and powders using a calibrated K-tron volumetric feeder.

Synthesis of blends was split into two steps.

i. Plasticization - Mixing soy powder (SC/SF) with glycerol to obtain plasticized soy (PSC/PSF)

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ii. Compounding - Mixing PSC with EPE in a given ratio to obtain an EPE:PSC blend.

The process is outlined here assuming the production of EPE and soy concentrate blend with glycerol as a plasticizer. A similar procedure was used when SF or ethylene glycol was used. While producing EPE:SC or EPE:SF blends the plasticization step was skipped.

PLASTICIZATION:

A fixed ratio of SC:GLY::70:30 was used based on the properties reported by Jane. Plasticization was done in two different ways to test different hypothesis about the mechanism of plasticization.

1. To obtain UNCMP PSC

SC and GLY were mixed in a kitchen aid mixer for 30mins to obtain a wet SC powder that was termed UNCMP PSC. Thus UNCMP PSC was obtained by ordinary mixing and was not exposed to high shear and high temperatures.

2. To obtain CMP PSC

SC and GLY were mixed in a kitchen aid mixer for 30mins and the wet powder obtained was extruded to obtain a more

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homogenized solid like brittle mass. Thus the CMP PSC was exposed to high shear and heat during plasticization.

The idea behind trying these two methods was to compare properties of blends obtained using CMP PSC and UNCMP PSC. If UNCMP PSC resulted in an insignificant loss of properties then it would save the cost of the extrusion during the plasticization stage. It would also mean that high shear and high heat are not required to attain adequate plasticization.

Whenever plasticization was carried out in an extruder, a flat temperature profile of 135C-140C was used. Screw speed was fixed at 125rpm. Torque of about 65% was observed during processing. A vent port was used in zone 5 (Figure 2) to get rid of volatiles generated. Different screw configurations were tried during this step. The brittle solid mass of PSC obtained was ground in a BTP granulator.

COMPOUNDING

EPE pellets were mixed with ground PSC in the desired ratio. This mixture was fed to the extruder and compounded.

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A flat temperature profile was used in all runs. Two different temperatures tried were - 135C and 170C. Different screw configurations with varying kneading capacities were examined. A fixed screw speed of 125rpm was used. Torque of about 55% was observed.

The discharge in the form of strings was quenched in a water bath, dried using air wipes and then pelletized. The pellets were further dried before injection molding or film casting in a 58C room for atleast 24 hours.

Hypothesized reactions:

Plasticization:

Acidic groups in protein + HO- groups in glycerol ---→ PSC

Compounding:

Unreacted HO groups in the PSC + HOOC groups in EPE →
EPE:PSC blend

Figure 2 - Schematic of the processing steps.

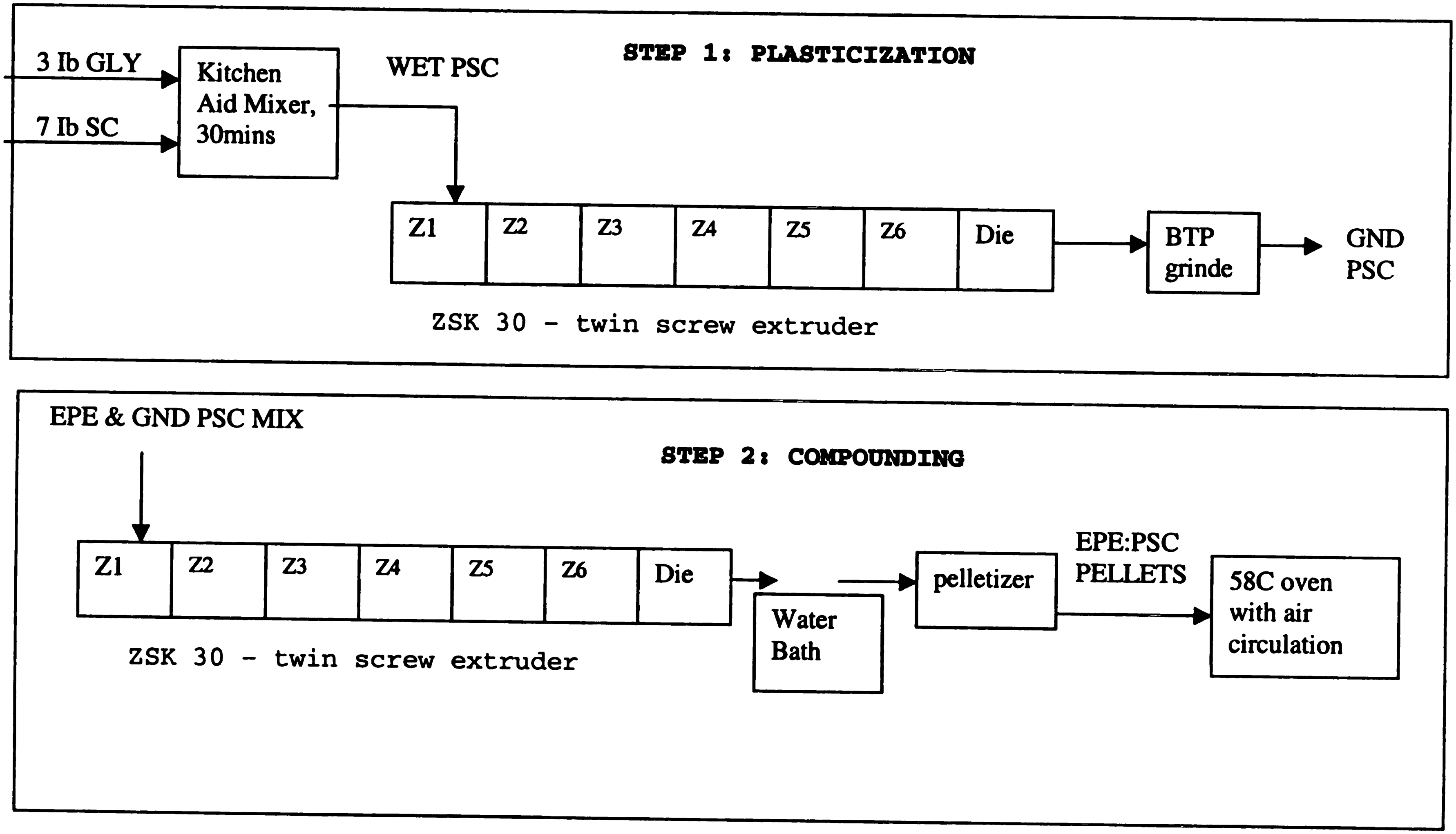

Figure 2 - Schematic of the processing steps.

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4.B INJECTION MOLDING

A Cincinnati Milacron injection-molding machine was used to prepare all D638 tensile test specimens from dried blend pellets. No mold temperature control was available. Hence, the mold temperature was at ambient.

Mostly flat temperature profiles were used, with temperatures ranging from 275F-360F in the screw barrel zones. The machine was operated in a single cycle mode because of occasional sprue sticking problems. A decrease in melt temperature or a 60-second cooling time was found to be adequate to avoid sprue sticking. A brief study was made of effect of reduction in cooling time on properties in an effort to reduce cycle times.

4.C FILM CASTING

Film casting was done using the Killion single screw extruder and film cast line (Appendix A). The EPE:PSC pellets were melted at about 300F, and a melt shaped by a film die was cast in the gap between the nip rolls. Positive cooling of the nip rolls to temperatures below ambient was necessary to make highly oriented, thin films. Good quenching of the films inhibits melt crystallization

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and retains amorphous domains, which are required for orientation and transparency.

The relative speeds of the main roll vis-à-vis the winder rolls controlled the draw ratio and film thickness. Increasing the speed of the winder for a constant main roller speed increased tension, hence orientation and also reduced film thickness. The film thickness was further reduced by simultaneously increasing the roller speed and the winder speed. Typically a roller speed of 400 rpm and winder speed of 50-60rpm was useful in obtaining good films. Ability to draw uniform films also depended on the film die gap.

Increasing the extruder screw speed increased the discharge, allowing wider films and higher roller and winder speeds. Temperature increase decreases the viscosity, increases pliability and allows thinner films.

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5. CHARACTERIZATION TECHNIQUES

5.A TENSILE TESTING

Universal Tensile Testing machine was used to conduct both the D638 and D882 tensile tests. Samples were conditioned in an ASTM room at 25% R.H. and 25C for atleast 40 hours. Bars were tested as per the D638 standard. Films were tested according to the D882 standard.

For high elongation D638 samples a test rate 50% elongation per minute was used. Non standard conditions had to be used for samples with very high elongations to obtain failure within machine limits. For very high elongation samples the bars were cut to 2″ guage length (G. L.) and a test rate of 2″/min was used. For even higher elongation materials, the bars were cut to a G. L. of 1″ and a test rate of 2″/min was tried. To test a film sample - dimensions of 1″ by 4″ and test speed of 100%elongation/min was used

5.B. ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY

A Phillips ElectroScan 2020 Environmental Scanning Electron Microscope was used to determine the inter-phase homogenization, extent of adhesion and distribution of the

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soy- component in the matrix. X-ray scans were also used to obtain the elemental composition of a particular region to identify the two domains.

Sample Preparation: All samples viewed in the ESEM were prepared by cutting with a blade a portion of the fracture zone from tensile specimens taken to failure. Samples were mounted on aluminum disc. Pictures for a given composition showing uniformity were analyzed in juxtaposition with those showing regions lacking in uniformity.

Typical SEM Conditions used were - accelerating Voltage of 20 kV, GSED Gas sensitive electron detector, 2000 - 150 x magnification. Around 15-20 pictures, with resolution ranging from 10μm to 450μm were taken of each sample to ensure coverage of a wide enough area.

5.C DIFFERENTIAL SCANING CALORIMETRY

Traditionally, a shift in the glass transition temperature is taken as an indication of compatibility. But soy protein does not show a DSC-discernible glass transition. Only a single peak around 146C is observed, which has been attributed to denaturing. So this method could not be used to check for compatibilzation.

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A study of melting point depression with increase in the PSC content was conducted to check for miscibility. A continuous and slight decrease in the melting point indicates miscibility of polymer blends. A number of blends have been analyzed in this way (Nazabal J., 1995). The polymer-polymer interaction parameter, χ is also related to the melting point depression through the Nishi-Wang equation.

The Hoffman - Weeks equation relates the melting point, Tm and the annealing temperature, Tc.

$$T_{mb} = \eta T_c + (1-\eta) T^0_{mb}$$

It can be used to compute the η parameter and the equilibrium melting point, T^0_{mb}. The η parameter is a morphological parameter. If the value of η tends to zero it indicates stable crystals while η tending to 1 indicates unstable crystals.

The EPE:PSC(GLY) blends in the ratios 80:20, 70:30, 60:40 and EPE were analyzed. The experimental procedure used to determine the melting point depression and η parameter is:

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1. Sample was heated to 150C and held isothermally for 10mins to ensure that all existing crystallites melt. The polymer was then rapidly cooled at 20C/min to the crystallization temperatures. Annealing temperature of 40C, 50C, 60C, 70C were tried for various runs.
2. Sample was left isothermally at the Tc for 60mins, then rapidly cooled to below -50C and then heated at 10C/min ramp rate and the melting curve was recorded.
3. The melting temperature Tm was plotted against the annealing temperature, Tc. A line was fit to this data. The slope of the line was equal to η
4. Area under the melting peak was obtained using the DSC analysis software to get a measure of the enthalpy of fusion.

Another advantage of this study is the possibility of using the crystallization temperature which yields the highest enthalpy of melting and hence the highest crystallinity as a good temperature for cooling during injection molding or for post production annealing.

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6. PROCESSING PARAMETER - PROPERTY DEPENDENCE

Figure 3 shows the details of the route taken to obtain the dependence of properties on processing conditions. The EPE:SF and EPE:SC blends prepared in the early stages of experimentation had poor tensile properties. This was attributed to the lack of melt formation of the soy component. Similarity in viscosities of materials being blended is desirable (Potschke, 1997). Attaining a melt form of the soy component below its degradation temperature would make it easier to compound it with EP. Hence, later work was done using soy after plasticization to obtain a thermoplastic form.

A few inherent constraints and general caveats on the interpretation of the data generated are warranted.

- Soy concentrate in the form used contains numerous other components (Appendix B) and higher sensitivity to heat than most synthetic plastics. It is not easy to characterize the more complex behavior of soy proteins using techniques developed for synthetic plastics. Though there is a profusion of literature about the food like properties of proteins there is inadequacy of information about soy proteins as polymers.

- During tensile testing of some D638 samples, very high elongation was obtained. The jaw separation limit on the UTS prevented testing to failure. The data reported in such cases therefore do not reflect the ultimate properties, which are sure to be better.

- Film formability was tested under a small set of film casting conditions, since it in itself requires process optimization.

- Wherever not specified plasticization as well as compounding was done using hi KB screw configurations. When specific parameter comparison was made, a similarity in the rest of the parameters was maintained, unless otherwise stated.

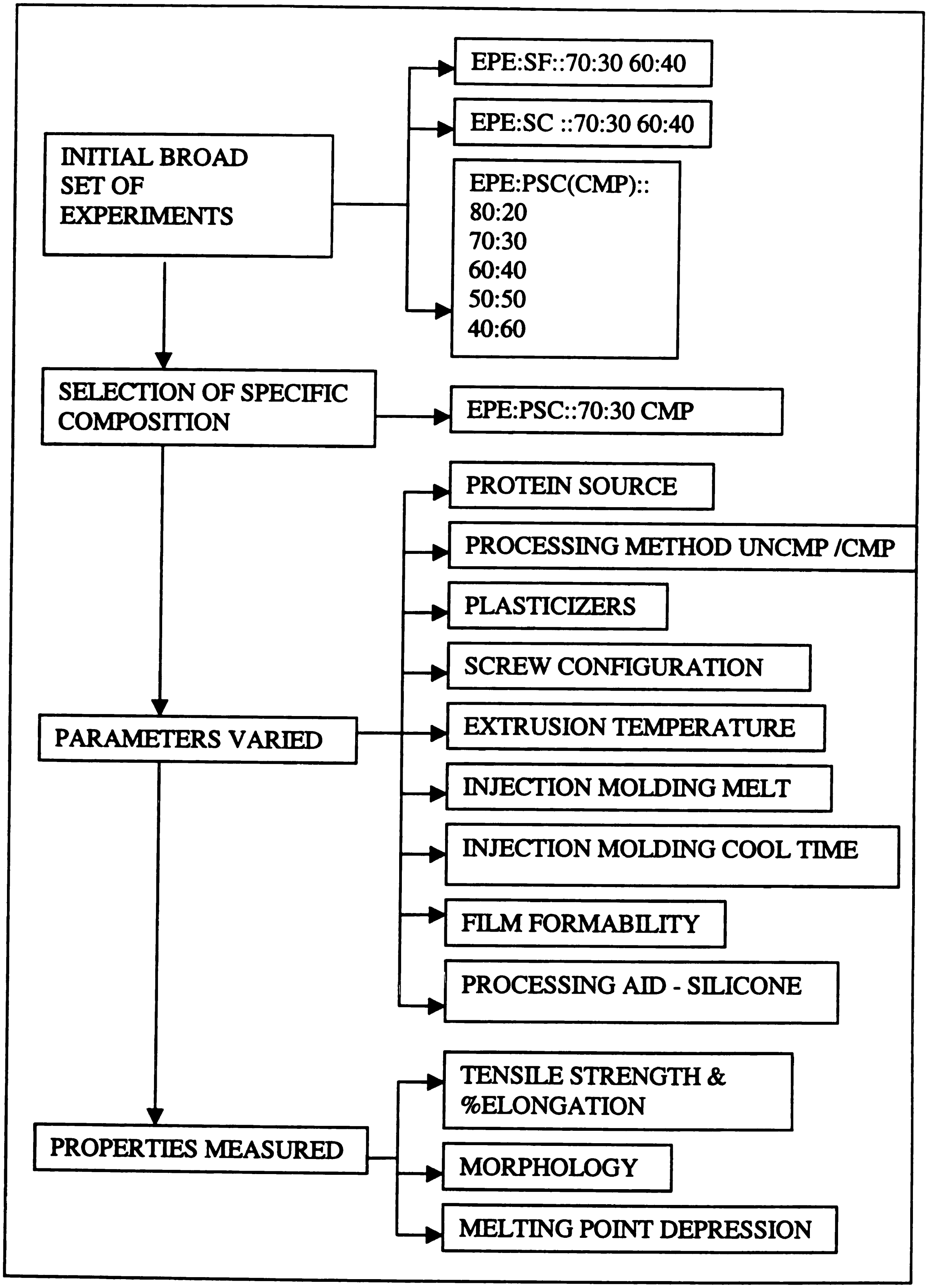

Figure 3 - Experimental Route

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6.A MECHANICAL PROPERTIES

6.A.1 EFFECT OF PLASTICIZATION

The presence of a plasticizer had a significant effect on the mechanical properties of the polymer (Figure 4). In fact, carrying out plasticization in an extruder was found to be important in promoting both tensile strength as well as %elongation at break. The difference between the CMP and UNCMP PSC is the duration and amount of exposure to heat and shear. Heat and shear denature proteins, exposing functional groups that become available for interaction. Processing under such conditions also increases the possibility of degradation of the protein, which may be favorable to a certain extent, if it were to increase the number of chain ends available for interaction.

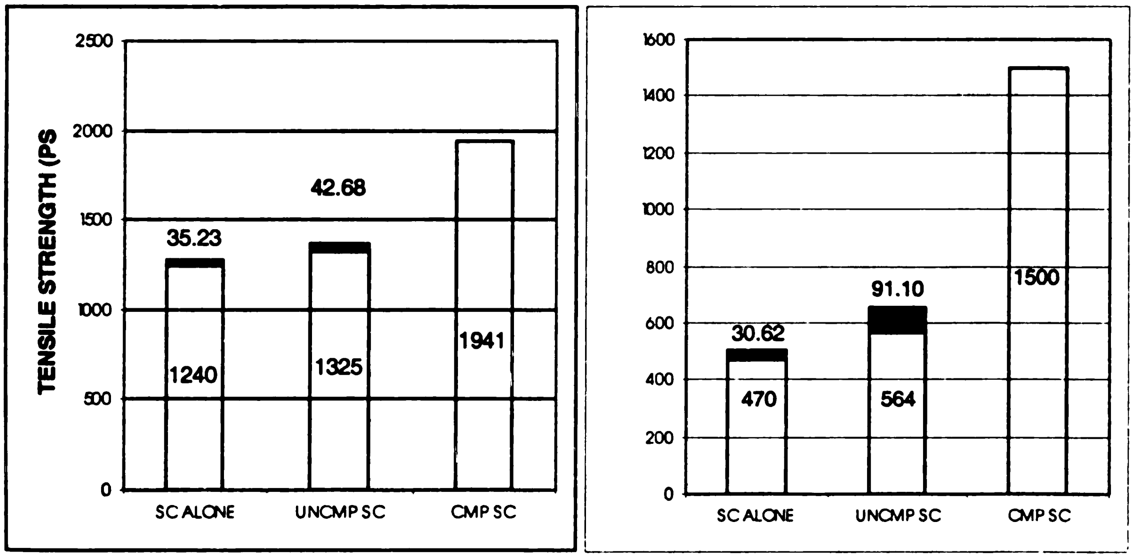

Figure 4 - Effect of plasticization with glycerol on EPE:SC::70:30 blends.

6.A.2 EFFECT OF BLENDING WITH SOY-PROTEIN SOURCES

Blending of EPE with SC slightly increased both tensile strength as well as percent elongation at break compared to blending with SF (Figure 5). This increase was more appreciable after plasticization, especially with regards to tensile strength.

The difference between the two sources is the percentage of protein each contains. This means increased presence of protein has a favorable effect on tensile properties of the blend. This can be explained if an increase in protein content leads to an increase in the interaction between the protein and EPE or decrease the unknown effect due to the non-protein components. The increased difference in tensile strengths after plasticization suggests that presence of glycerol had a significant role in promoting the protein-polymer interaction.

The percent elongation was not affected significantly by the use of either sources of protein.

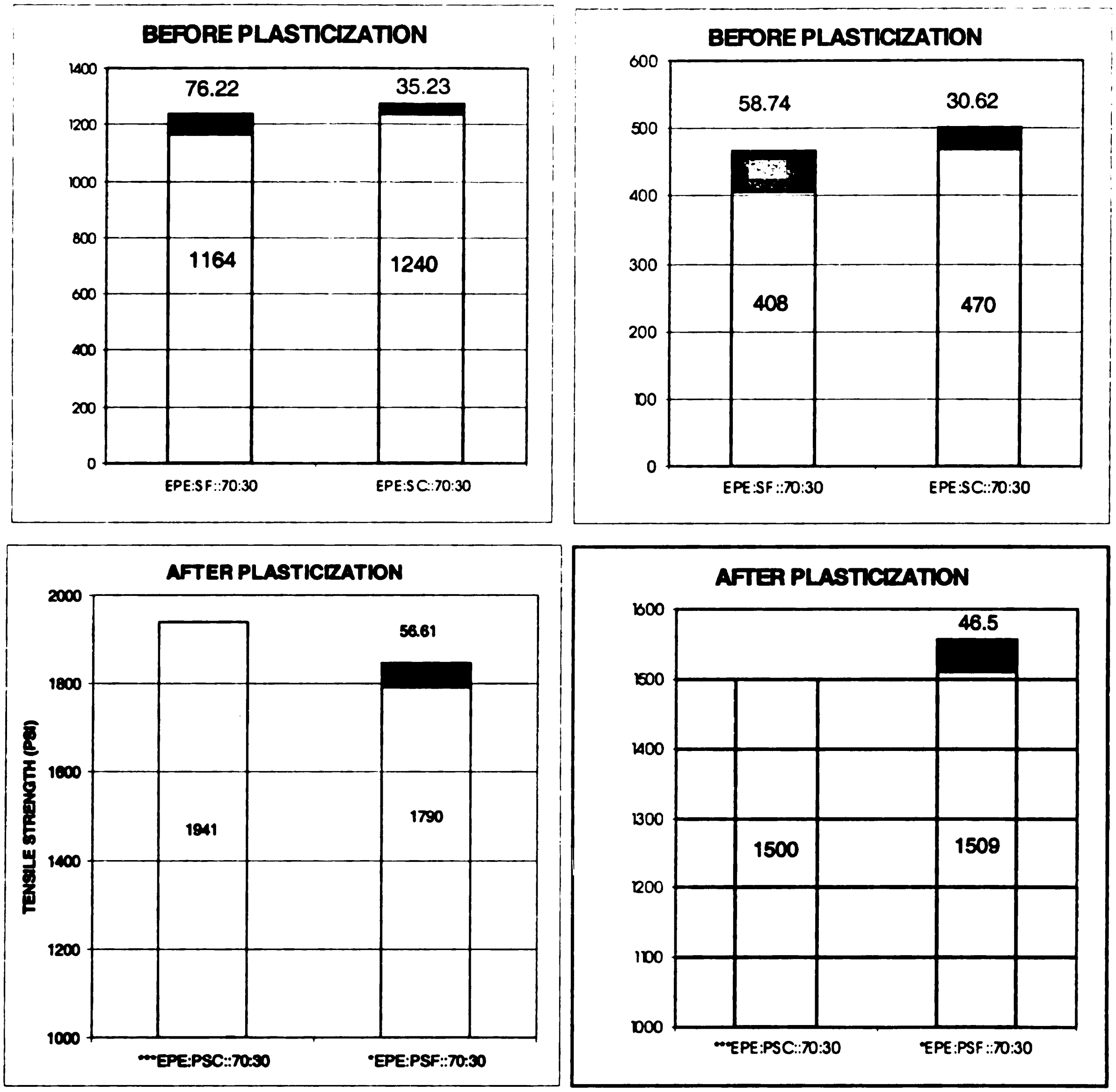

Figure 5 - Effect of using different sources of protein before and after plasticization with GLY on EPE:SOY PROTEIN::70:30.

6.A.3 EFFECT OF COMPOSITION

A decrease in the PSC weight fraction led to an increase in both tensile strength and %elongation at break (Figure 6). An increase in the PSC weight fraction above 40% led to a drastic degradation of both tensile strength and

%elongation to unacceptable levels. Compositions containing PSC below 40% weight were therefore studied in greater detail. It was due to better film properties obtained with the 70:30 composition that this composition was investigated more thoroughly compared to the 60:40 composition

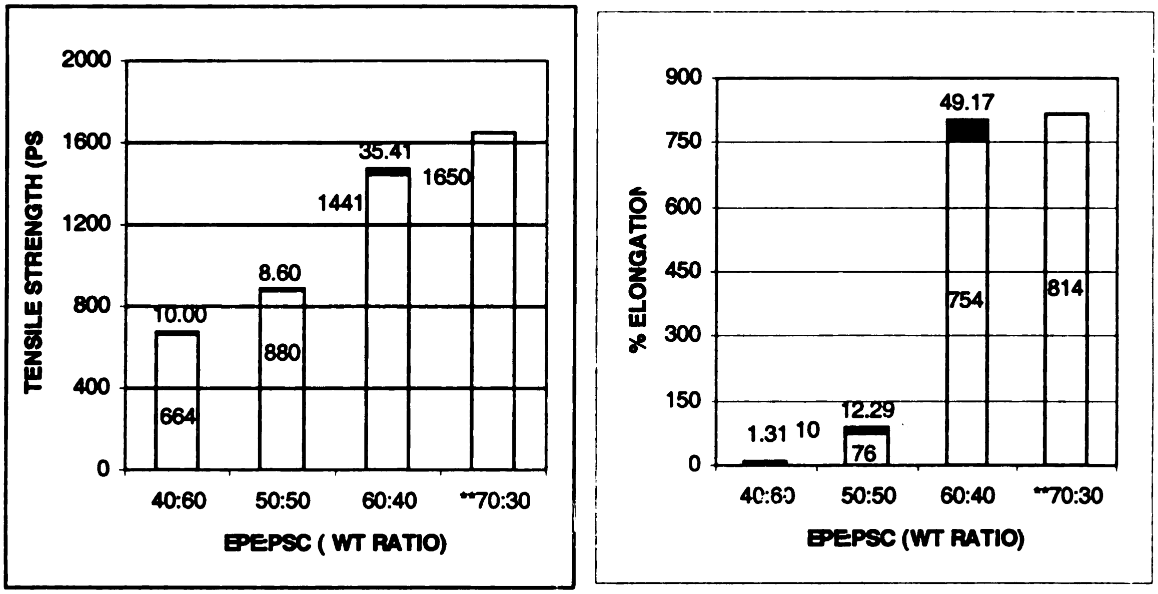

Figure 6 - Effect of varying weight fraction of PSC on EPE:PSC blends

6.A.4 EFFECT OF DIFFERENT PLASTICIZERS

Lower tensile strength and %elongation was obtained when ethylene glycol was used as a plasticizer instead of GLY (Figure 7). The differences in values are substantial. Processing difficulties were experienced during plasticization of soy concentrate with ethylene glycol as torque rose rapidly even at very low feed rates. This may be due to the inability of ethylene glycol to effectively plasticize soy concentrate and hence improve flowability.

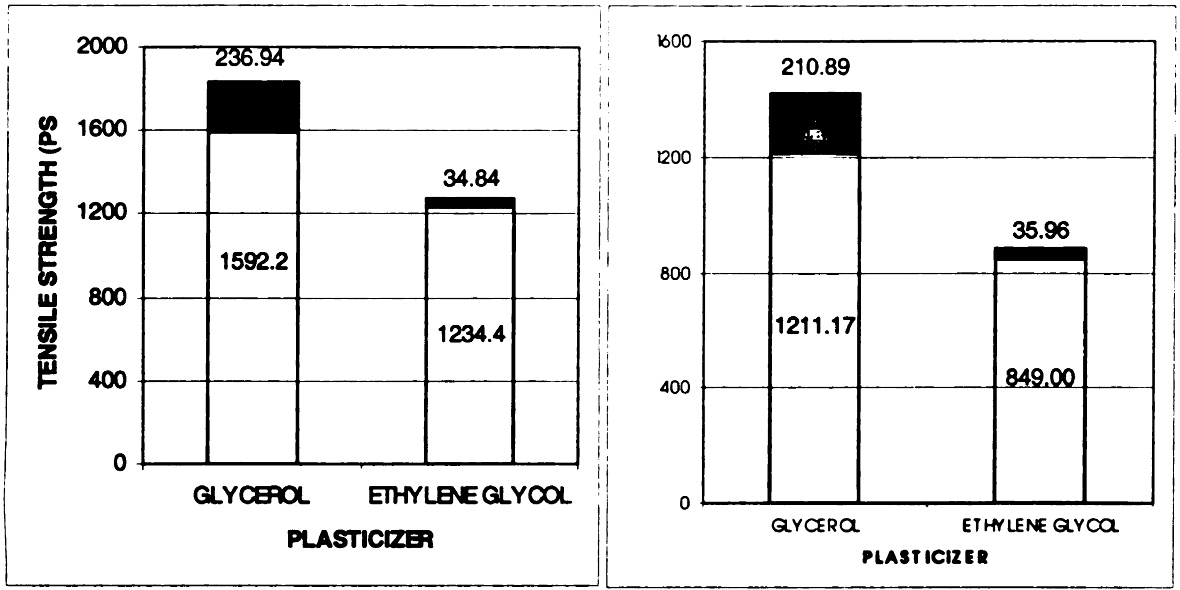

Figure 7 - Effect of different plasticizers on EPE:PSC::70:30 blends

6.A.5 EFFECT OF EXTRUDER SCREW CONFIGURATIONS

Three different screw configurations, shown in figures 8,9 and 10 were used. The screw configurations were classified based on the percentage of high shear kneading blocks present (Table 3). Four different combinations with different screw configurations used during the plasticization and the compounding steps were tried (Table 4). The location of the kneading blocks was fixed at approximately downstream of the feed zone. Optimization of the element positioning was not considered at this point.

TABLE 3 - BASE SCREW CONFIGURATIONS

NOMENCLATURE	KNEADING BLOCK AS %LENGTH OF TOTAL LENGTH
HI KB	31.41
MOD KB	19.44
LO KB	10.86

TABLE 4 - COMBINATIONS OF SCREW CONFIGURATION USED FOR PLASTICIZATION AND COMPOUNDING

CONFIGURATION	DESCRIPTION P- PLASTICIZATION,	 C-COMPOUNDING
C1	P- LO KB,	C- LO KB
C2	P- LO KB,	C- HI KB
C3	P- MOD KB,	C- HI KB
C4	P- HI KB,	C- HI KB

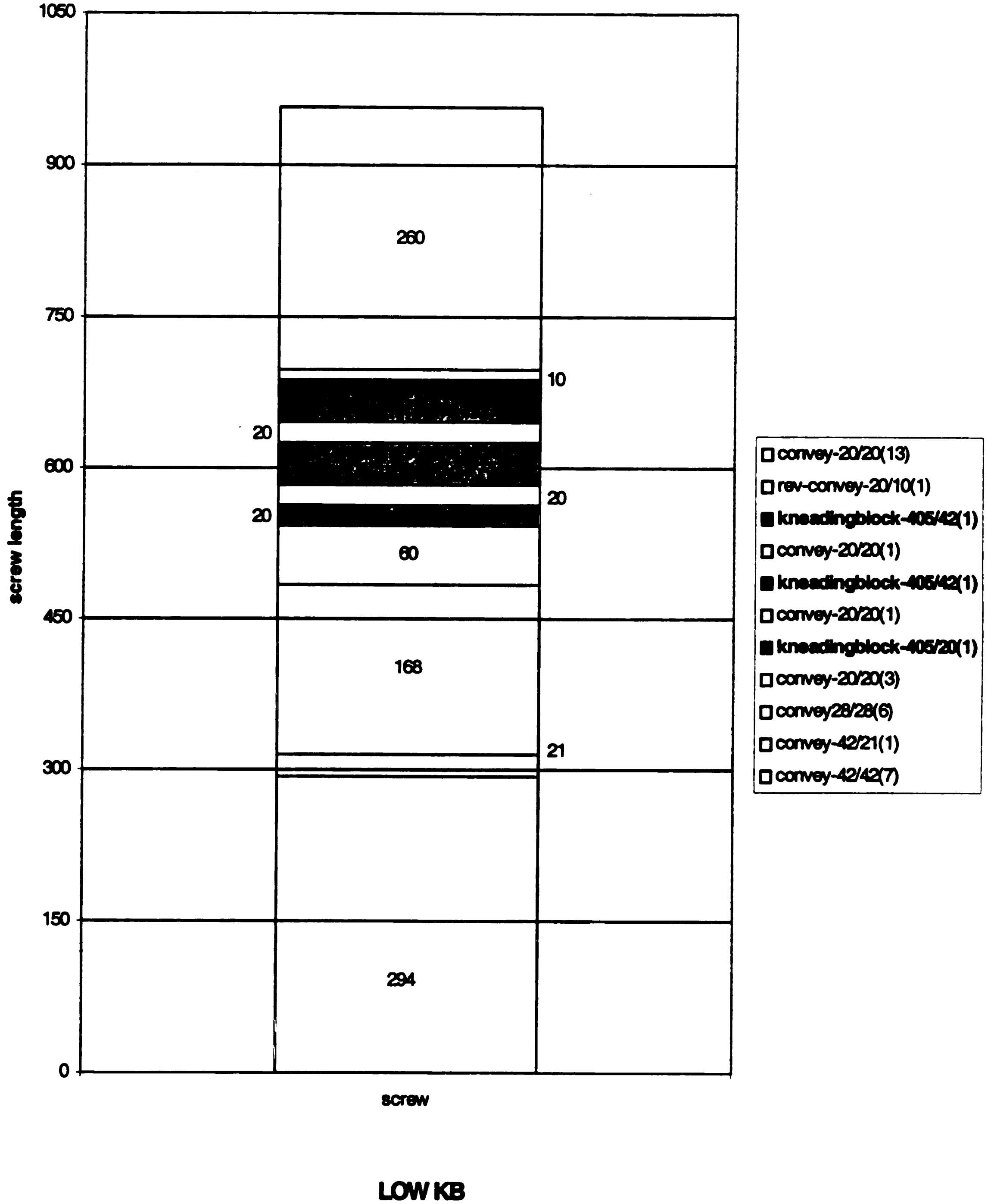

Figure 8 - Low KB screw configuration

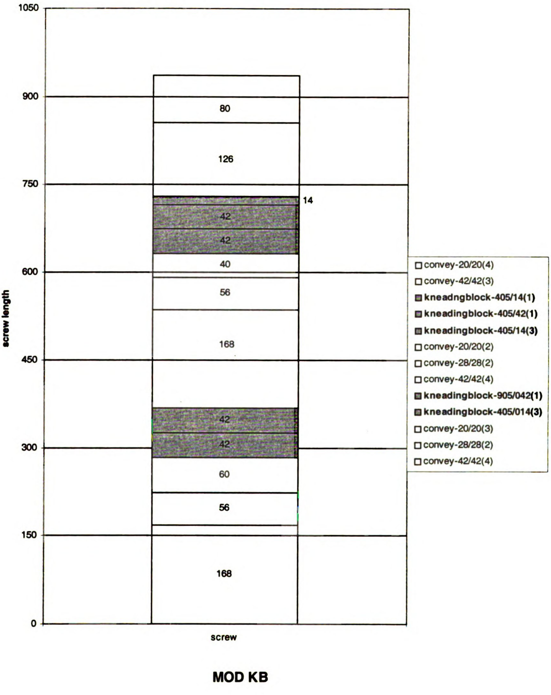

Figure 9 - C2 Moderate KB screw configuration

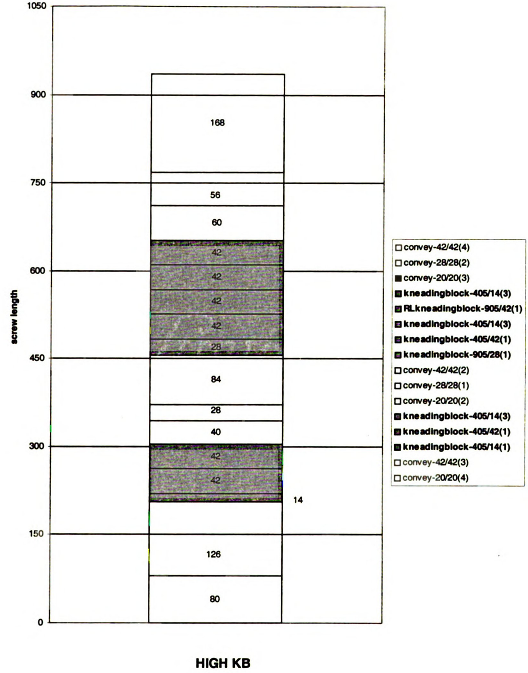

Figure 10 - C3 High KB screw configuration

Screws with lower kneading capability have a higher conveying capability, lower torque and power requirement. Hence they are preferred from the productivity point of view. Increasing the kneading blocks leads to better mixing and hence mechanical properties. However, it can also lead to degradation of temperature sensitive materials like SC. A compromise screw configuration is needed to solve the conflicting needs of higher productivity and energy requirements versus those for obtaining good mixing and hence better product quality.

Tensile properties were found to be highly sensitive to the screw configurations used (Figure 11). It was observed that both tensile strength and percent elongation improved with increase in the kneading blocks used.

The importance of using a moderate to high shear screw during plasticization is especially clear when properties for the C2, C3 and C4 are compared. C2, C3 and C4, all use high KB screws for compounding and three different screws for plasticization. The differences in the properties can now be explained on the basis of the differences in screw configurations used during plasticization. An increase in the kneading capability of the screws used during plasticization led to an improvement in both tensile strength and percent elongation. Thus both high shear and heat are necessary during plasticization in order to obtain good interaction between the two components.

SC plasticized using low KB screws and then compounded with high KB screws had slightly lower tensile strength than that obtained by using low KB screws during compounding (c1, c2). The difference however is within error bounds, suggesting that use of moderate to high KB screws during plasticization stage is necessary. Use of high KB screws during compounding does not make up for use of low KB screws during plasticization stage.

Overall use of high KB screws during both plasticization and compounding resulted in the best tensile strength and %elongation.

This emphasizes the need for thorough mixing of SC and plasticizer using both heat and shear, which can be achieved best in an extruder. Heat and shear therefore seem significant in property improvement. As stated elsewhere, heat and shear lead to denaturing of proteins, exposing functional group. Thus, if an increase in functional groups is causing an improvement in tensile properties, it follows that there must be some positive interaction between the plasticized protein and EPE.

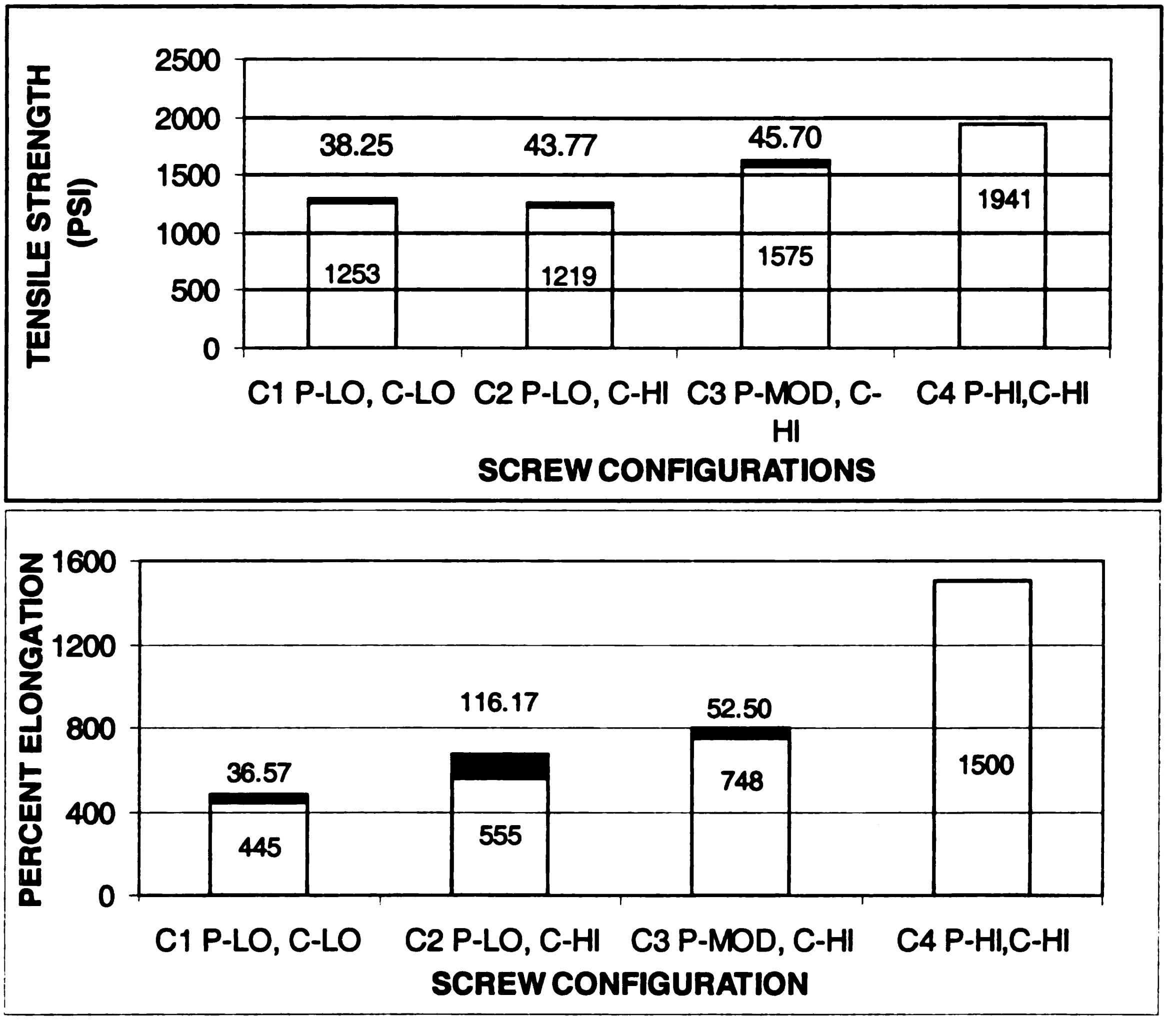

Figure 11 - Effect of screw configuration on EPE:PSC::70:30 blends

6.A.6 EFFECT OF THERMAL HISTORY

Compounding of EPE with PSC was carried out at two different temperatures - 135C and 170C. Each of these blends (E135C and E170) were injection molded at two different temperatures 135C and 160C (I135 and I160).

Among the blends injection molded at 135C, the E170 blend had higher tensile strength and %elongation. While among those injection molded at 170C, the E135 blend had higher tensile strength (Figure 12 and 13).

The materials extruded at 135C when injection molded at 160C gave the highest tensile strengths. Blends extruded at 170C and injection molded at 135C gave the second highest. The lowest properties occurred when the material was both extruded and injection molded at 135C and the next lowest when the material was both extruded and injection molded at 160C.

This could mean that exposure of the compound to higher temperatures during atleast one of the processing steps is required to obtain better properties. However exposure to high shear and heat during both steps is detrimental. Thus, there seems to be an optimum exposure to high temperatures.

Since during extrusion the material is subjected to severe shear stress compared injection molding, simultaneous imposition of high temperature may be leading to excessive degradation of the protein and hence loss of properties.

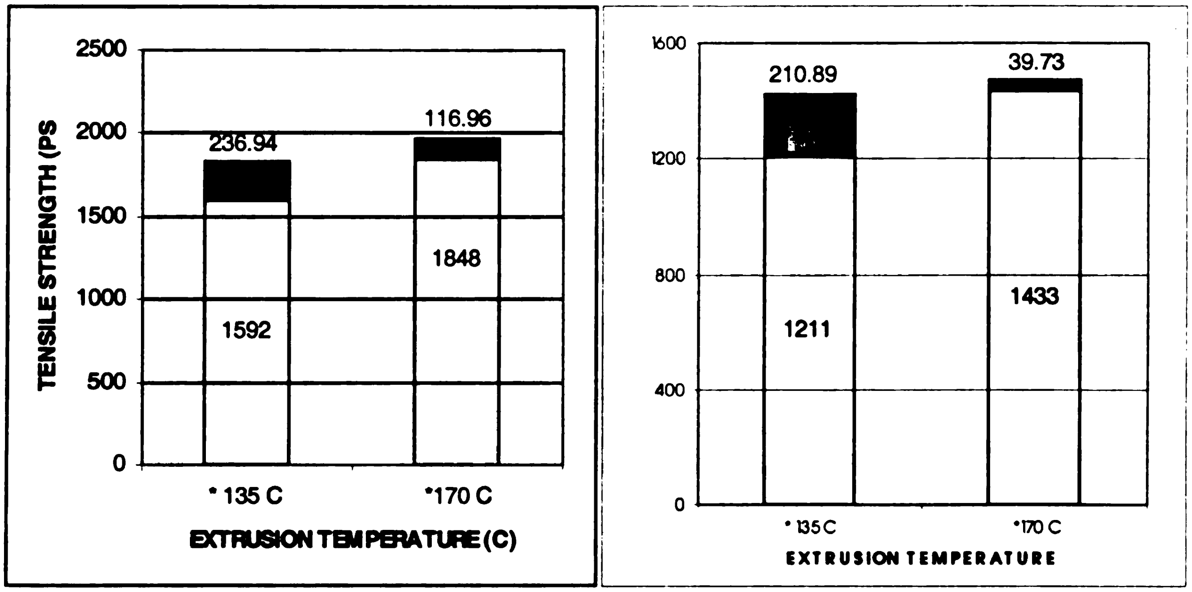

Figure 12 - Effect of extrusion temperature on EPE:PSC::70:30 blends injection molded at 135C

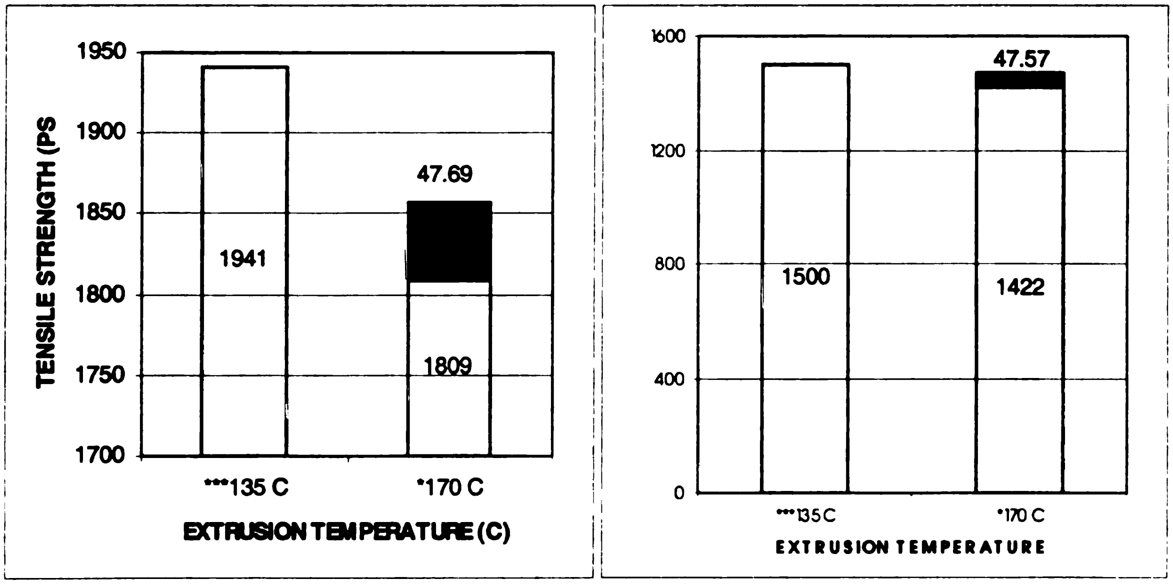

Figure 13 - Effect of extrusion temperature on EPE:PSC::70:30 blend injection molded at 160C

The above discussion shows that the properties are an aggregate effect of the thermal history imposed by both the processing steps extrusion and injection molding.

A material with lower thermal history during compounding resulted in higher tensile properties when subjected to higher temperatures during injection molding and vice-versa. However the decrease in tensile strength when the material was subjected to high temperature during both steps was not very high. Thus, higher temperatures lead to better properties than lower temperatures.

The ideal combination is the use of lower temperatures (around 135C) during compounding and higher temperatures (around 160C) during injection molding

6.A.7 EFFECT OF DURATION OF COOLING DURING INJECTION MOLDING

A decrease in cooling time during molding is important to reduce cycle times and increasing productivity during injection molding. Two cooling times were tried during the injection molding of EPE:PSC(GLY)::50:50. Halving mold cool time from 60s to 30s had negligible effect on the tensile strength as well percent elongation. A higher cooling time at an appropriate temperature is expected to allow better crystal growth thus improving tensile properties. Since the loss in mechanical properties is negligible a 30s cooling time seems adequate.

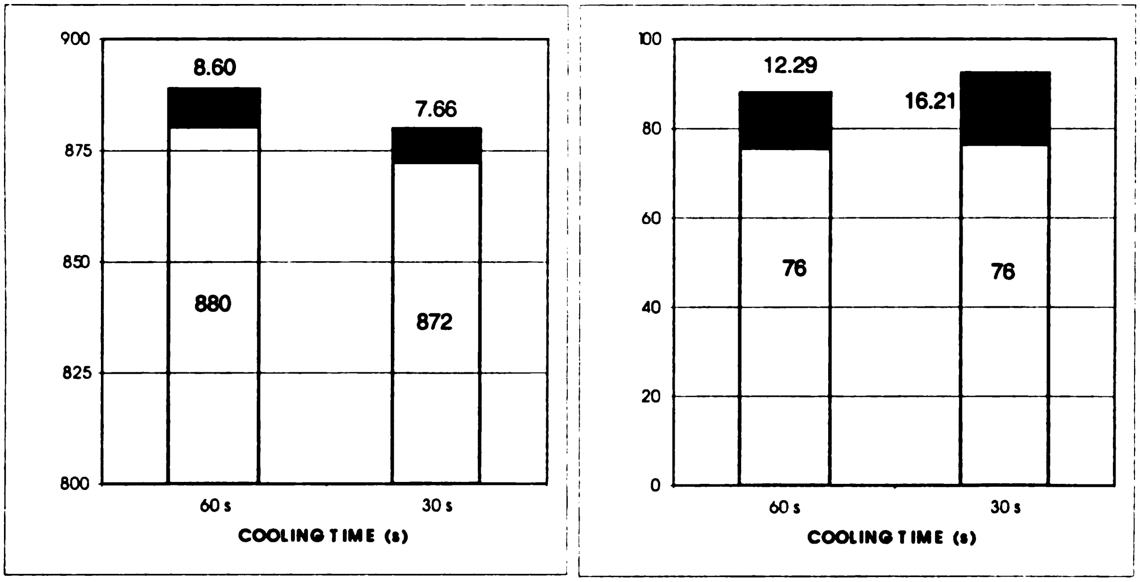

Figure 14 - Effect of duration of cooling on EPE:PSC::50:50 blend.

6.A.8 EFFECT OF COMPOSITIION ON FILMS

Film were cast from materials plasticized at 140C, compounded at 135C with a MOD KB screw during plasticization and HI KB screw during compounding. Films had a thickness of around 10 mils. Films obtained were translucent suggesting miscibility. An improvement in tensile strength was obtained when compared to the data reported by Eastman. However, work to check repeatability could not be conducted. Adding silicone had very little effect on the tensile strength of the films. It however improved the processbility of the EPE:PSC::60:40 blend.

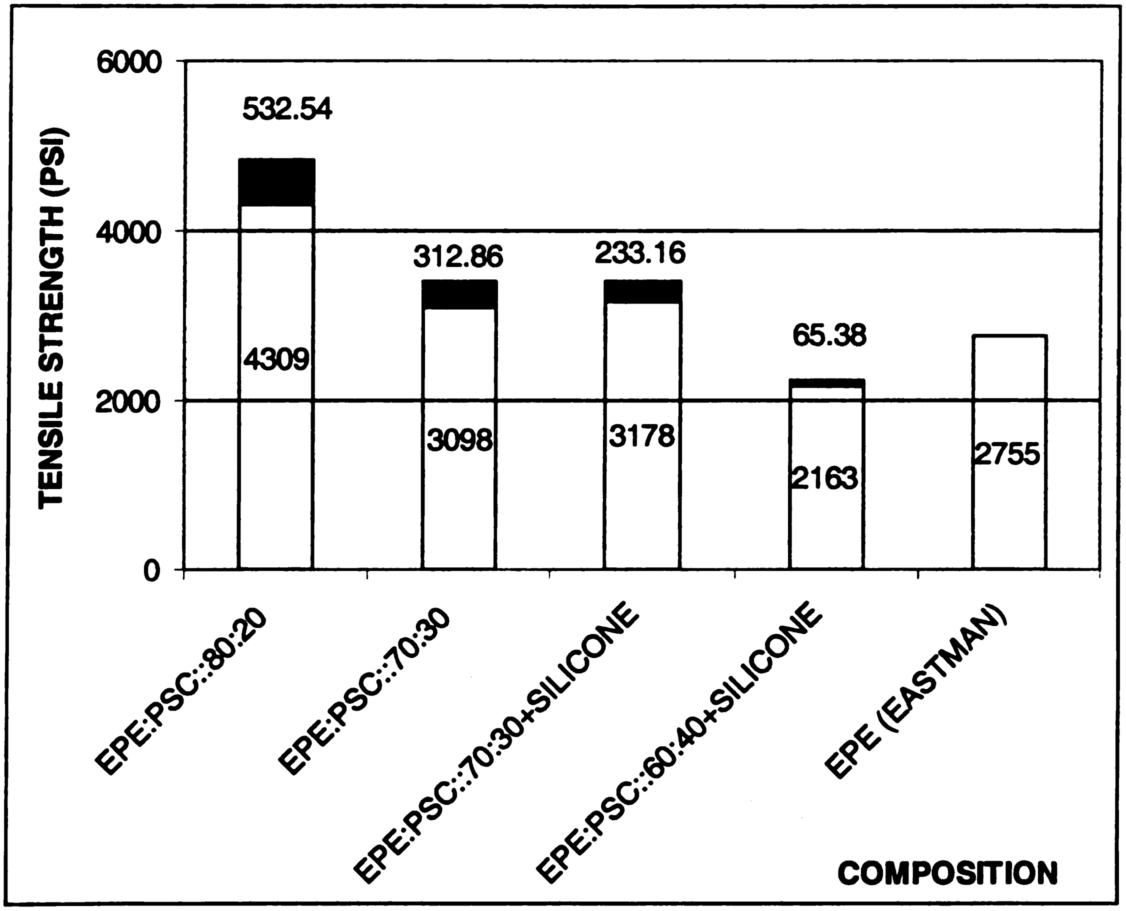

Figure 15 - Effect of composition on film tensile strength (D882)

6.B MORPHOLOGY

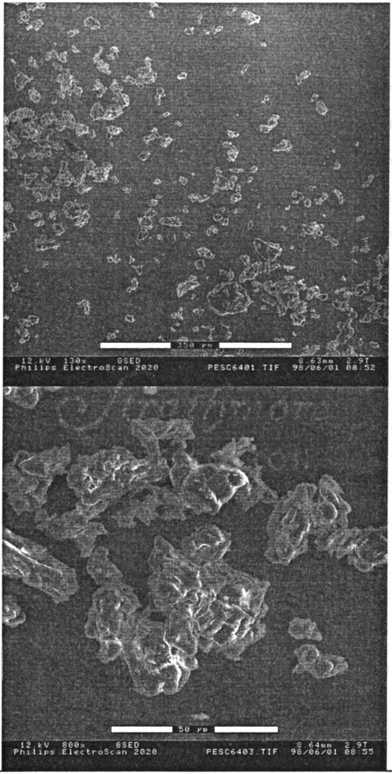

Figure 16 - SEM pictures of soy concentrate particles. Top: A very wide particle size distribution can be seen. Bottom: Very irregularly shaped soy-particles

Soy concentrate particles shown in figure 16, have irregular shapes and a wide particle size distribution. Bigger particles appear to be aggregates of smaller ones. Particles have sharp edges. All blend pictures that follow show some common features. Since tensile fracture specimens were used the EPE matrix underwent ductile failure through yielding in the form of fibers. The differences were in the adhesion, particle sizes, particle size distribution and dispersion.

EPE:SC::70:30 E135C resulted in a very distinctly phase separated blend. From figure 17, it can be easily appreciated that good mixing was not achieved, with particles showing practically no adhesion to the matrix. Failure occurred through yielding of the matrix alone in the form of fibers with no participation of the soy-concentrate particles. In fact, the almost free hanging particles with sharp edges could be acting as obstructions limiting the extension of EPE during the yielding process. This could lead to a reduction in the maximum elongation attainable and consequently the tensile strength. Also, a wide particle size distribution is seen. The largest particle detected was about 70µm.

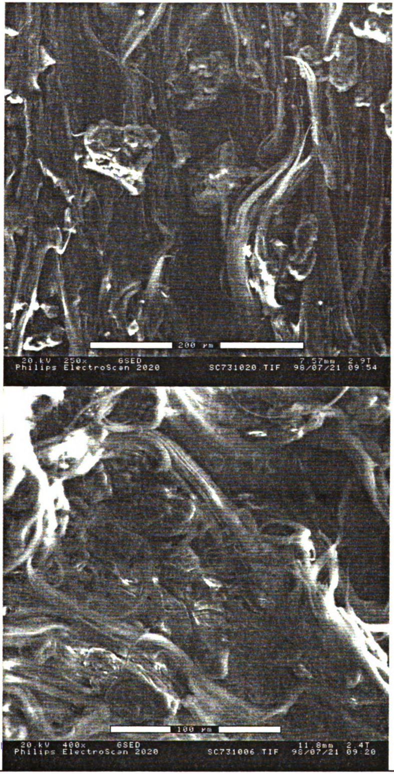

Figure 17 - SEM picture of EPE:SC::70:30. Very poor adhesion between matrix and particles, also very large 50-70µm particles exist

6.B.1 EFFECT OF PLASTICIZATION ON SOY CONCENTRATE

Plasticized soy-concentrate when compounded with EPE (EPE:PSC::70:30 E140C) yielded the morphology in figure 18. On visual inspection the PSC particles appeared as dark brown, very brittle and glassy materials in the interior with a soft rough outer surface. In the blend, PSC particles show a better adhesion to the matrix and a finer dispersion compared to the EPE:SC::70:30. The particles are coated by the matrix better than in the case of the EPE:SC blend. Phase separation is still present, but the particle boundaries are slightly less distinct and very slightly smeared. This may be due to the wetting or solvation of soy concentrate particles in the surface region leading to interaction with EPE. However, PSC does not seem to have melted or fused with the EPE matrix. Particle size distribution is improved vis-à-vis the EPE:SC blend but there is still noticeable variation and room for improvement. The largest particles detected were in the range of 10-15µm. Also, the distribution of the particles in the matrix is not very uniform.

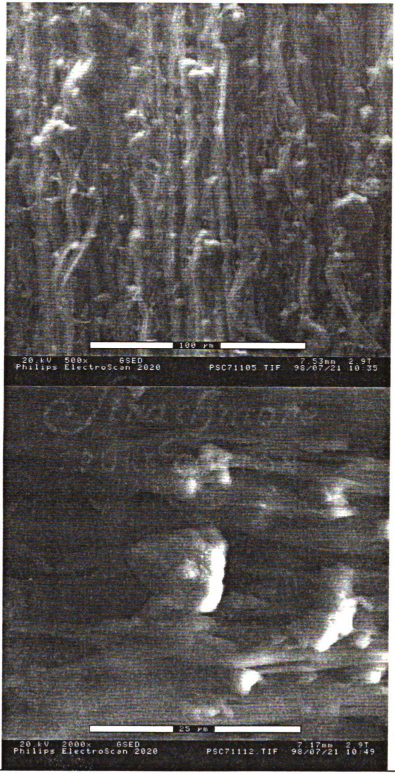

Figure 17 - SEM picture of EPE:PSC(30GLY) E140C, I120C. Tensile fracture zone. Slightly better adhesion. Distribution is uneven and there is room for improvement.

6.B.2 EFFECT OF PLASTICIZATION ON SOY FLOUR

Compounding EPE with (UNCMP)PSF(GLY) was attempted to achieve cost reduction since a certain level of success had been obtained using soy-concentrate. But inter-phase homogenization could not be achieved as can be seen in figure 19. The largest particle seen was about 25um. Almost no adhesion was observed. Most particles were not even coated. But this may be due to the use of PSF that had not been plasticized in an extruder. Lack of plasticization in the extruder seems to give ineffective mixing. A study EPE:(CMP)PSF should yield a better morphology.

Figure 19 - SEM picture of EPE:(UNCMP)PSF(G)::70:30. Very poor adhesion. No coated particles

Four compositions of EPE:PSC(G)::70:30 were prepared by extruding at E135C and E170C and each of these compositions was injection molded at two different temperatures I135C and I160C.

EPE:PSC(G)::70:30 E135C I135C shown in figure 20, had a number of soy concentrate particles in the form of clusters leading to a very non-uniform dispersion. A number of particles seem to be coated but not smeared which would have meant some amount of dissolution. The particles appear to be of a finer size with most particles below 5µm. This blend showed the lowest tensile strength of the four compositions.

EPE:PSC(G)::70:30 E135C I160C shown in figure 21, has a very narrow particle size distribution as well as uniform dispersion within the matrix. A number of particles appear to be smeared and well coated with the matrix. Also the particle size is below 5µm. Smearing suggests some amount of interaction or dissolution of the PSC particles in the matrix, atleast at the surface. Sharp edges are hardly noticeable. This blend showed the highest tensile strength.

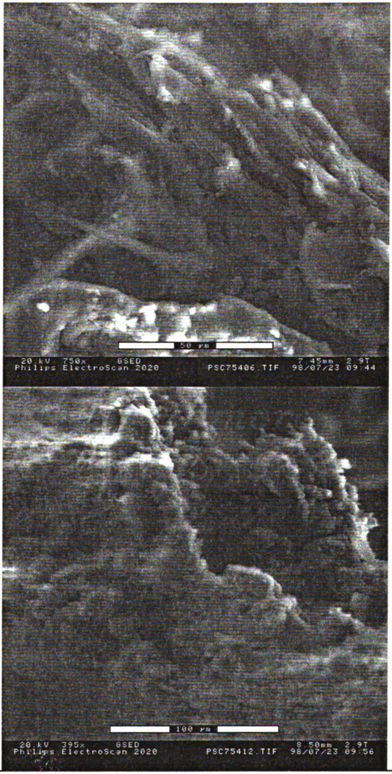

Figure 20 - SEM picture of EPE:PSC(G)::70:30 E135C I135C. Clusters or particles and a very non-uniform distribution of matrix are seen.

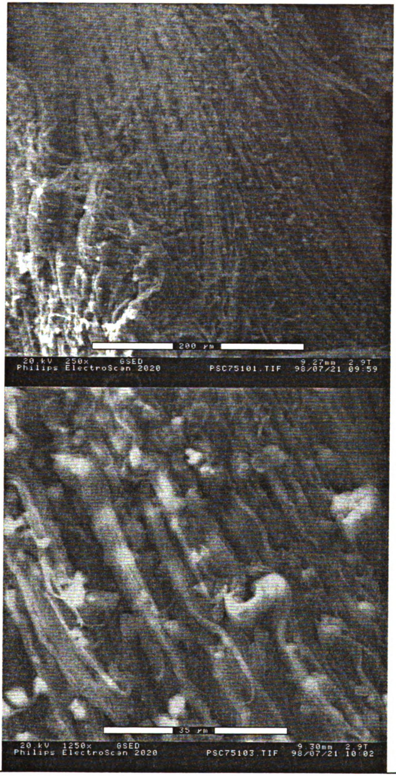

Figure 21 - SEM picture of EPE:PSC(G)::70:30 E135C I160C. A very uniform particle size distribution accompanied by reduction in particle size to less then 5um. Particles are well coated and smeared.

EPE:PSC(G)::70:30 E170C I135C is shown in figure 22. PSC particles seem to be well coated though not particularly smeared with most particles below 5μm. The adhesion between the particles and the matrix seems to be excellent since the matrix is stretching into thin fibers without disconnecting from the particles. However some variation in particle size and clustering of particles is noticeable.

EPE:PSC(G)::70:30 E170C I160C shown in figure 23, has uniform particle size distribution. The particles are also very well coated and dispersed. A little smearing of particles leading to indistinctness of the particle boundaries is observable.

Increase in temperature usually leads to a decrease in viscosity and hence an improvement in flowability, making good mixing possible. This should lead to an improvement in tensile properties. The improvement in morphology of the E170 I160 blend was not accompanied by a similar improvement in tensile properties. This can be explained if use of high temperature during both compounding and injection molding were to cause degradation of the protein molecules.

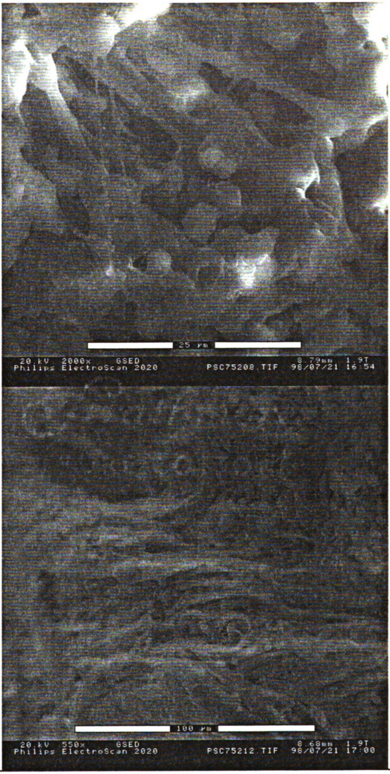

Figure 22 - SEM picture of EPE:PSC(30GLY)::70:30 E170C I135C. Particles are strongly adhering to the matrix even though the matrix itself is yielding. Non-uniform distribution of particles within the matrix is visible

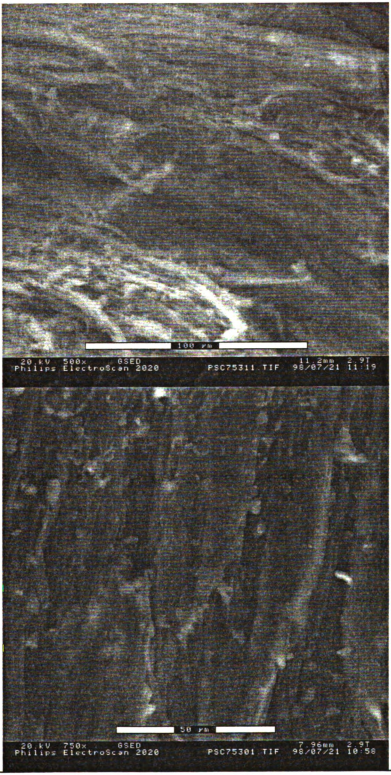

Figure 23 - SEM picture of EPE:PSC(G)::70:30 E170C I160C. A uniform size distribution and a certain amount of smearing visible. Particles are well coated.

6.B.4 CONCLUSION

Low temperatures during both compounding and injection molding leads to clusters and non-uniform dispersions. Simultaneous use of higher temperatures during both the steps leads to a reduction in particle size and uniform morphology, though it may also have been accompanied by degradation of soy protein. Use of low temperature during compounding and high temperature during injection molding led to increase in the smearing of the PSC particles in the blend, with fine particle size distribution.

Low adhesion was observed in EPE:(UNCMP)PSF(G) blends. Passing PSF through the extruder during plasticization to form (CMP)PSF should yield better results.

Above all the effect of how well plasticization was carried out during the formation of PSC and PSF can have a significant effect on the properties after compounding. It is not clear from these pictures whether what has been termed as PSC or PSF is indeed a thermoplastic material. Since the PSC seen in the images had a very particulate nature, it is likely that the material was cross-linked due to the -OH groups in glycerol. But the smearing seen in some of the blends and the persistence of the coating even after material was stretched to failure seems to suggest a certain amount of dissolution or at least interaction between the three blend components, namely -SC, GLY and EPE

6.C DIFFERENTIAL SCANNING CALORIMETRY

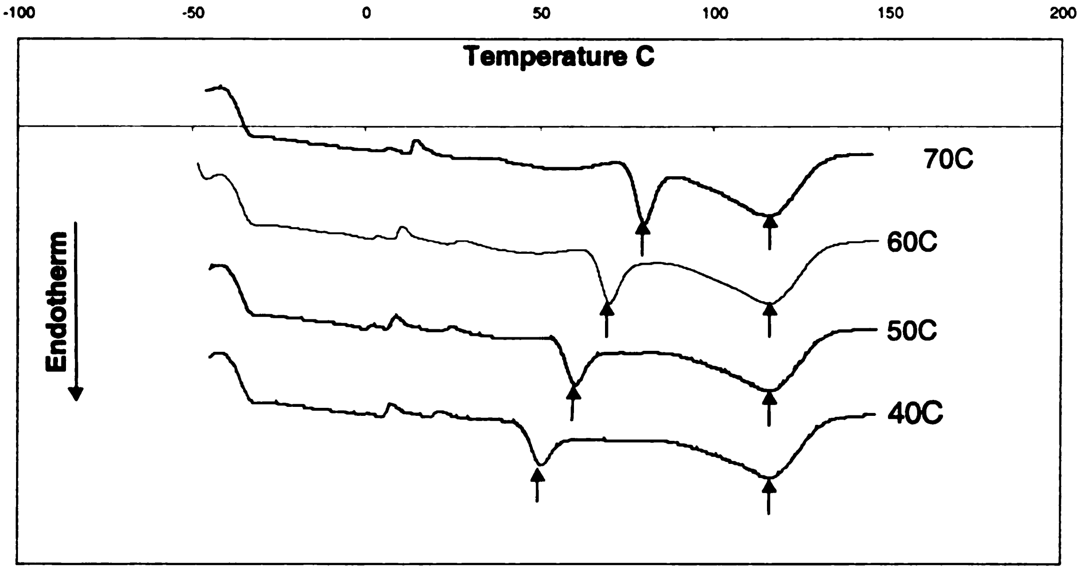

Figure 24 - Enthalpy versus Temperature of EPE

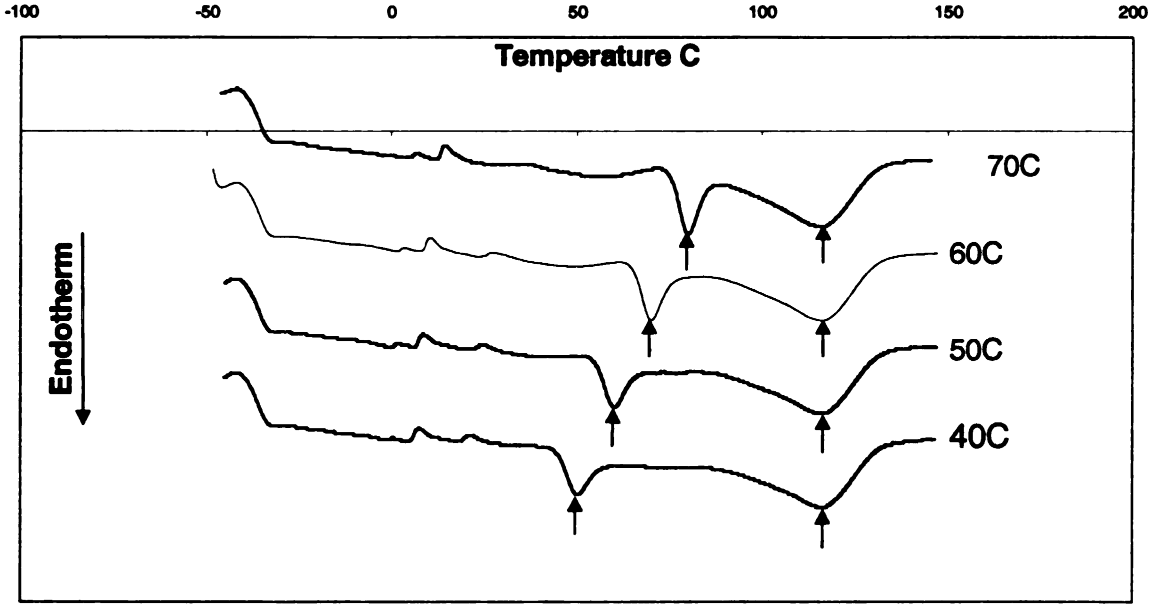

Figure 24 - Enthalpy versus Temperature of EPE

6.C.1 DUAL MELTING BEHAVIOR

Figure 24 shows the dual-melting behavior of EPE. This phenomenon is observed in all its blends with PSC. The explanation for this behavior is usually the development of two different crystal species during crystallization. This is a very common phenomenon in case of copolymers (Kim, 1997).

6.C.2 EFFECT OF ANNEALING TEMPERATURE ON MELTING POINT

As can be seen from figure 25 the multiple melting characteristic is dependent on the annealing temperature, particularly, the melting temperature of the lower melting peak. As the annealing temperature increases the lower melting crystals rearrange to be part of the crystals with higher melting point. This is possible when the lower melting peak is caused by the crystallization of smaller, highly mobile molecules.

Increase in melting point is usually a sign of increase in crystal size (Kim, 1997). The increase in the melting point of the lower melting peak can thus be attributed to an increase in the crystal size, with eventual merging with the larger higher melting crystals.

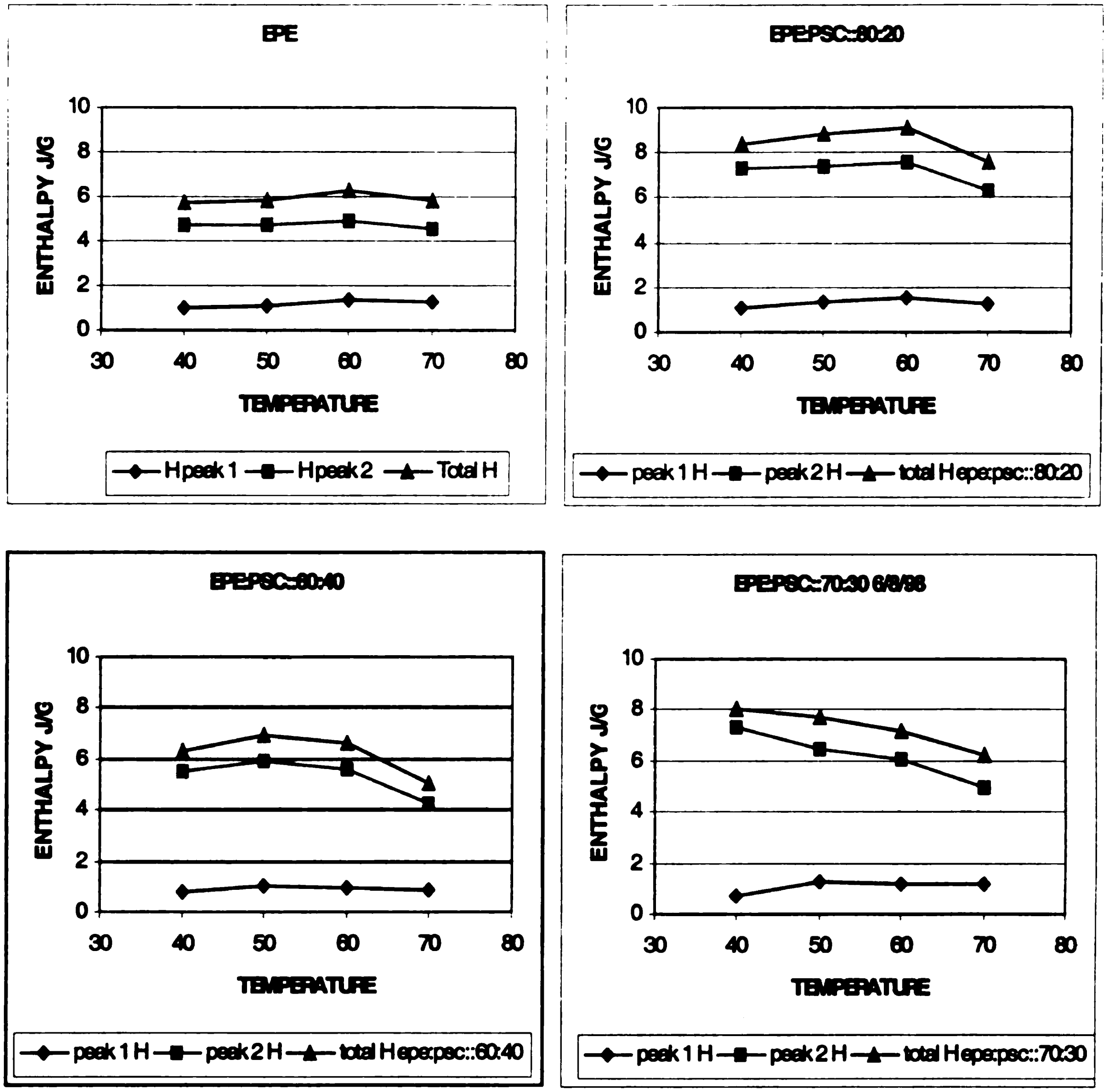

Figure 26 - Enthalpy versus annealing temperature for four different compositions

6.C.3 EFFECT OF ANNEALING TEMPERATURE ON CRYSTALLINITY

Figure 26 shows the enthalpy of fusion for the various compositions as a function of the annealing temperature. The enthalpy of fusion is a direct measure of crystallinity. Thus it can be seen that the total crystallinity. Thus it can be seen that the total crystallinity of the compositions studied, show a maxima in the temperature range of 40-70C. The only exception was the 70:30 blend.

The enthalpy of fusion for the lower melting peaks is much lower then the enthalpy of fusion of the higher melting peak for all the compositions. Thus, the higher melting peak is the major contributor towards the total crystallinity in the polymer.

Each composition had a different temperature at which the maximum heat of fusion and hence crystallinity was obtained. As can be seen from figure 26, with increasing PSC content, a decrease in the annealing temperature increases the crystallinity.

TABLE 5 - Effect of varying composition on the heat of fusion:

Composition	**Temp at max total H**	**Total H J/g**
EPE	60C	6.231
EPE:PSC::80:20	60C	9.087
EPE:PSC::70:30	40C	8.062
EPE:PSC::60:40	50C	6.946

The total enthalpy of all the blends considered was higher than that of EPE alone. Among the blends there was a decrease in the highest enthalpy with increase in the PSC content. This can be explained if an increase in the PSC fraction may be hindering crystal growth.

There are two possible explanations for higher heat of fusion of the blends over that of the EPE. The increase in the heat of fusion can be attributed to either denaturing of soy proteins, which escaped unaffected during processing or an increase in the crystallinity due to PSC fraction aiding crystallization.

Denaturing would be likely if the heat of fusion increased with increasing soy concentrate fraction. But this does not happen. The other possibility is that the plasticization induced mobility of the soy protein molecules causes them to participate in the crystallization process in some kind of formation of co-crystalline domains. At the very least the PSC particles may be acting as nucleating agents.

To summarize, increasing the annealing temperature increases the melting point of the lower melting peaks. However the crystallinity has a maxima at some intermediate temperature. This temperature can therefore be used for injection mold cooling or for post forming annealing to improve crystallinity and hence mechanical properties.

6.C.4 EFFECT OF COMPOSITION ON THE MELTING POINT

A depression in melting point of the higher melting peak with an increase in the PSC weight fraction is observable. However, there is no appreciable effect of composition on the melting point of the lower melting peak. As the annealing temperature decreases, the depression in melting point of higher melting peak with increase in PSC content is more impressive. There is no similar effect in the melting temperature of the lower melting peak even at different annealing temperatures.

The η values obtained by fitting Hoffman-Weeks equation to the melting temperature versus annealing temperature plots for different compositions are listed in the table 6. According to theory, a value of $\eta = 0$ implies perfect crystals while $\eta = 1$ reflects inherently unstable crystals. Thus the lower melting peak is on account of unstable crystals while the higher melting peak is due to stable crystals.

TABLE 6 - Hoffman Week's η parameters obtained by linear regression of Tm peak vs. Tc data

Composition	η for peak 1	η for peak 2
EPE	0.9957	-0.0197
Epe:psc::80:20	0.9829	0.0315
Epe:psc::70:30	0.9822	0.0661
Epe:psc::60:40	0.9895	0.0007

The significance of this discussion is that a melting point depression in the higher melting peak, arising from perfect crystals with increase in the amorphous phase can be taken as an indication of miscibility.

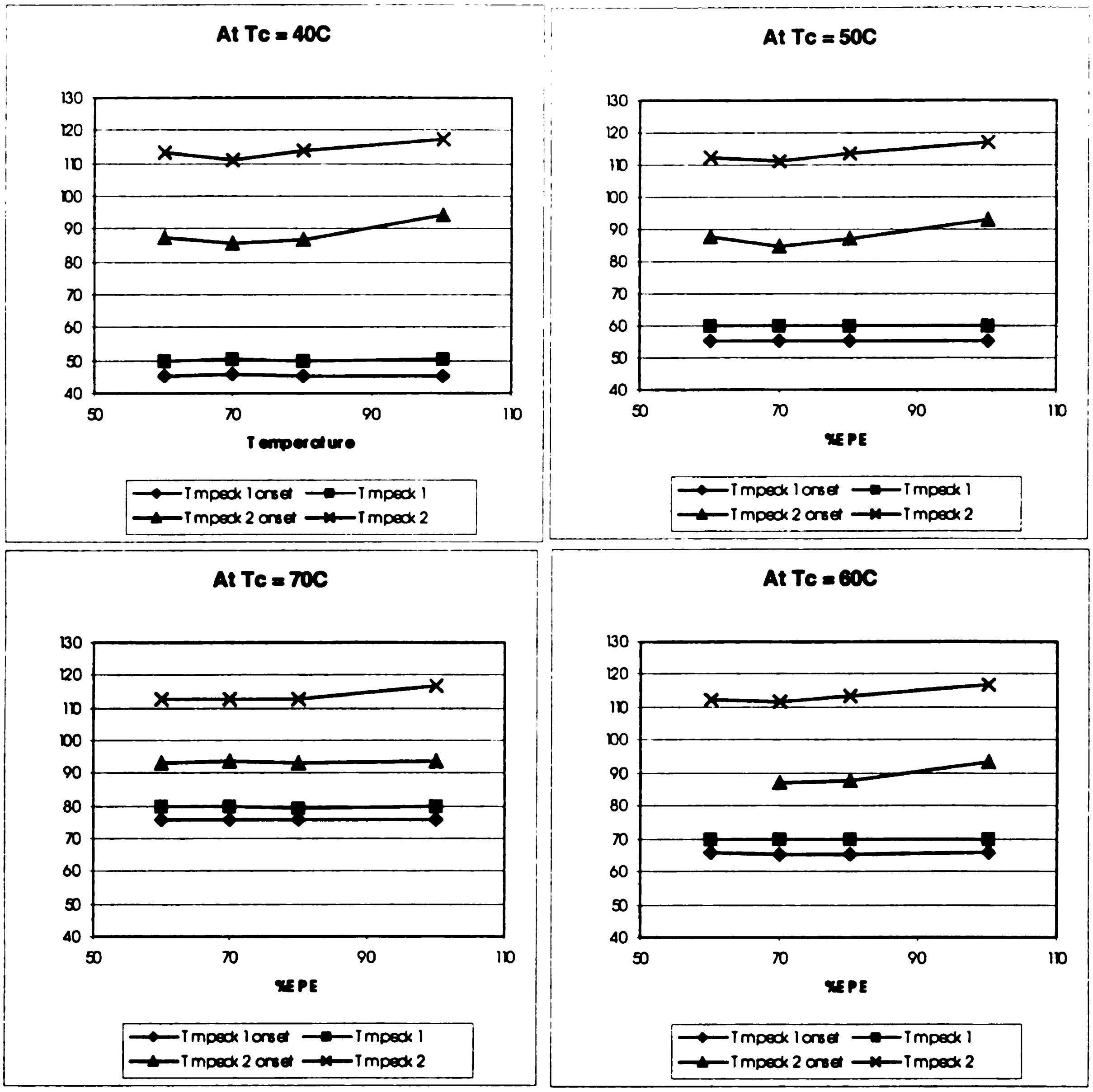

Figure 27 - Melting Temperature vs. composition for different annealing temperatures

6.C.5 EFFECT OF PROCESSING TEMPERATURE ON MELTING POINT

Figure 28, shows melting temperature depression obtained for 70:30 blends processed at different temperatures during compounding. The run 1 and run 3 materials were compounded at 135C while the run 2 material was compounded at 170C. Both blends prepared at 135C show a higher decrease in the melting point of the higher melting peak compared to that of the 170C blend. Among the two 135C materials the run 1 material had slightly higher depression in melting point. Thus conditions used during run 1 were more conducive to inducing miscibility. PSC used in run 1 was made at 140C while PSC made for run 3 was made at 135C. Thus the slightly higher temperatures during plasticization is beneficial, though it is very close to the accepted soy protein degradation temperature. The tensile properties of run 3 materials are better then those of run 2. (Tensile strength of run 2: 1808psi and run 3:1867psi, both being injection molded at 160C and produced using the same screw configurations).

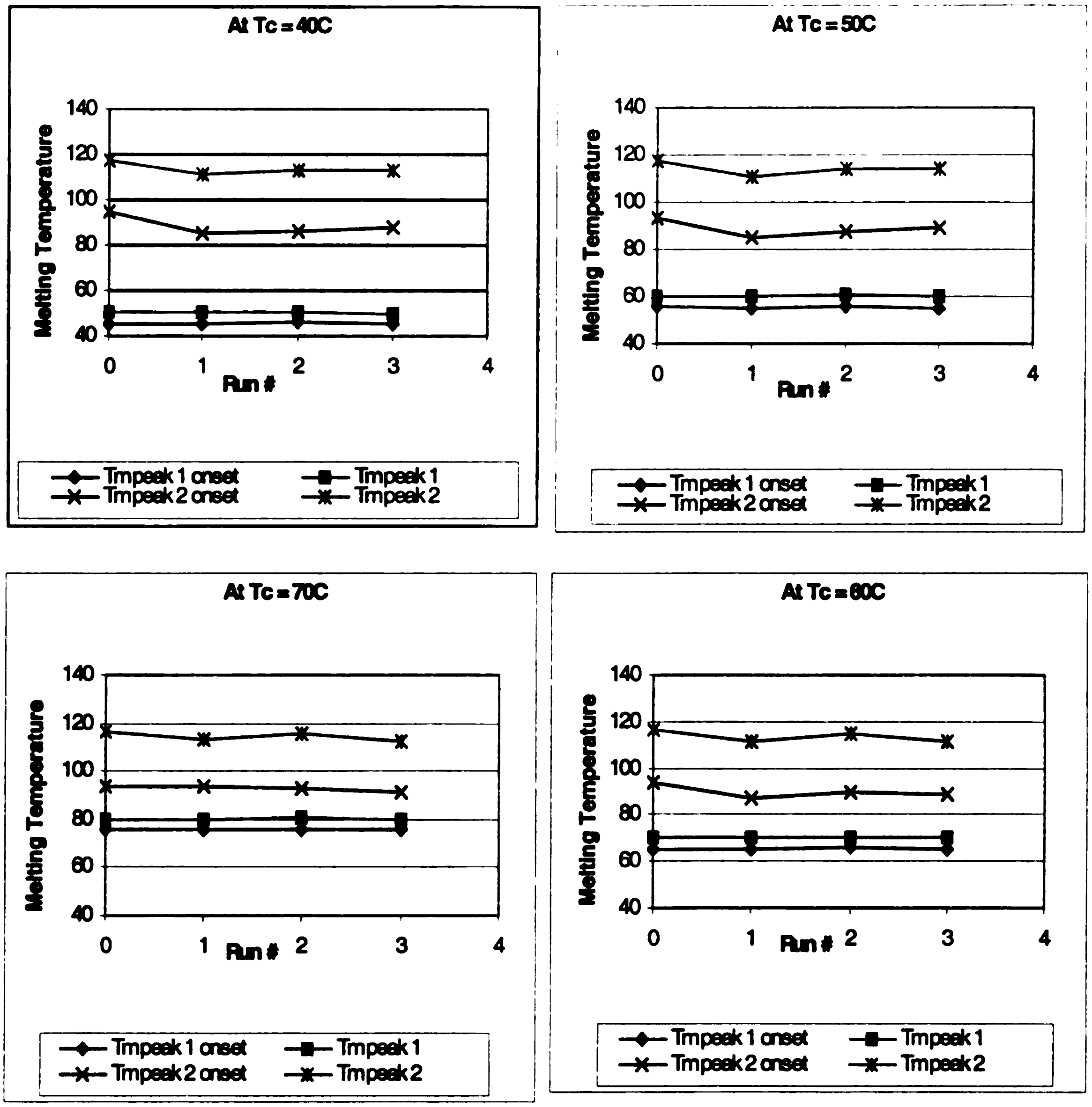

Figure 28 - Effect of processing temperatures on the melting point depression for EPE:PSC::70:30 blends

6.C.6 CONCLUSION

From the melting point depression it appears that there is some miscibility in the EPE:PSC blends. The melting point depression was higher for EPE:PSC::70:30 blends compounded at 135C. Thus, 135C seems to be a more suitable temperature to use during compounding.

Use of annealing temperature depending on the composition, as listed in table 5 can lead to increased crystallinity in injection molded articles.

The differences in the melting points are small. Hence the data need to be cautiously interpreted with respect to reliability.

7. SCALE UP

A process flow diagram for annual production of 2.5 million lbs. of EPE:PSC(GLY)::70:30 is shown in figure 29. The plant consists of two extruders in series. Extruder, E1 is for plasticization of SC with glycerol and E2 is for compounding of the PSC with EPE. Storage is provided for the 3 raw materials SC, GLY and EPE and the final product, assuming a 15-day inventory. Carbon steel containers and gravimetric feeders are used for powders and pellets. A pump, PU is used for GLY. The PSC produced in E1 is pelletized by P1 before being fed to E2. The final product EPE:PSC::70:30 is cooled in a water bath, B air dried using a twelve inch air wipe, pelletized by P2 and then conveyed to the product storage. Feeders and conveyers are omitted from the process flow diagram for simplicity.

Some of the assumptions made were that the drive power used to rotate the screws was used to distribute and mix the two materials, while the heat supplied was used for fusion. An approximation was made which equated the heat requirement to the heat of fusion of the materials, since the enthalpy required for temperature change is relatively small. Usual material balances were used to compute the raw material needs. Other assumptions are shown in Table 9.

Extruder sizing:

Traditional scale-up strategies for extruder sizing are so detailed and notation so difficult that its usefulness is somewhat lost. A simple scale up theory based on the work of Pierre H. M. Elemans (Elemans, 1988) was therefore used.

During scale up, all quantities of interest are expressed as a power of a characteristic ratio, such as the screw diameter ratio (Figure 30). Depending on the scaling strategy (geometrical, thermal - laminar, thermal - mixed annular) chosen a certain set of parameters (L/D, Brinkman number, Graetz number, P-number, B-number) are unaltered (Figure 31).

These ratios can be combined with the governing equations for mass transport, power consumption and mixing to obtain relations between their powers using dimensional analysis (Figure 32). Depending on the strategy used for scale up, that is what parameters are held constant a set of scaling exponents are calculated for each quantity (Table 7).

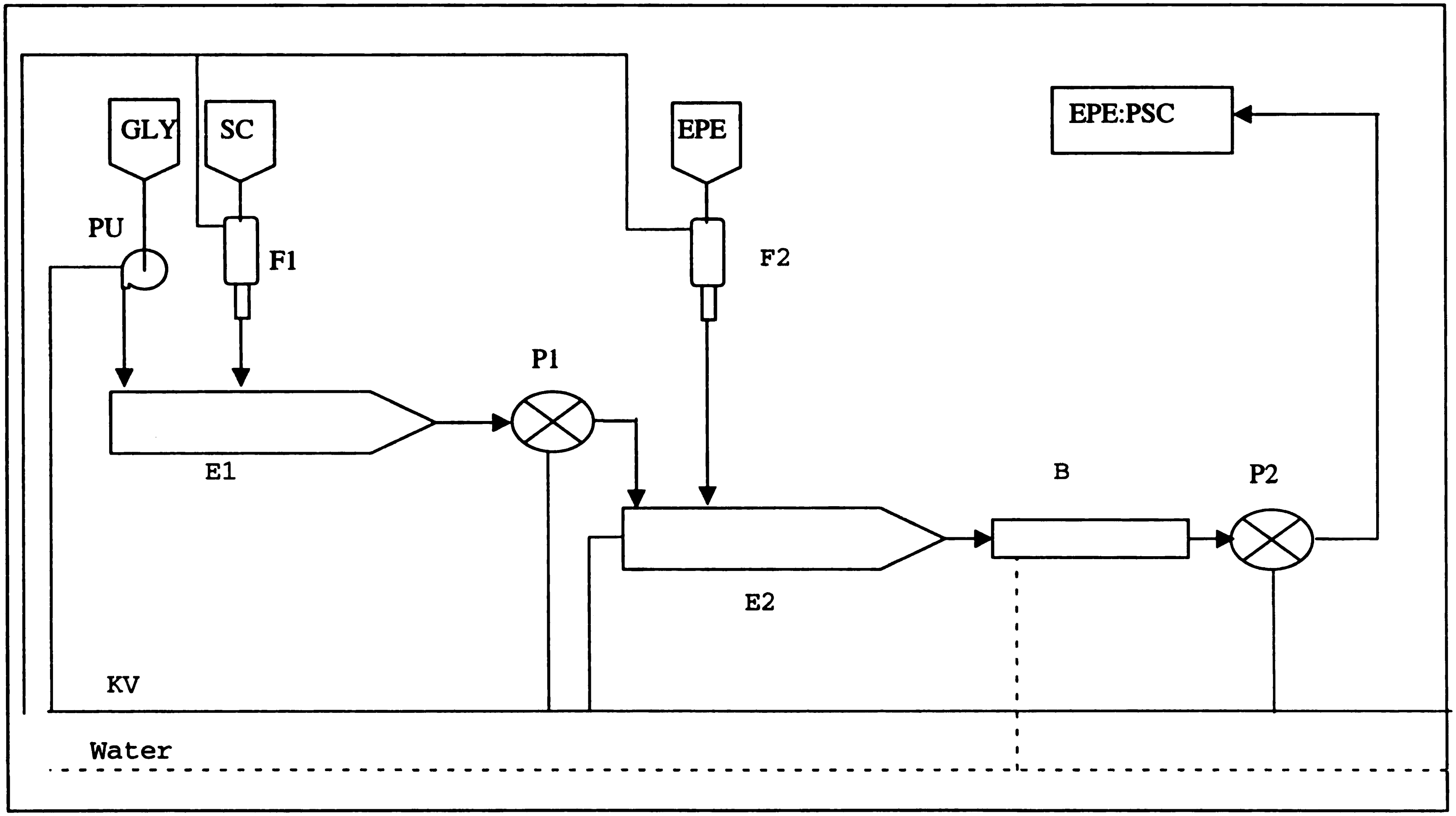

Figure 29 - Process Flow Diagram

For the present calculation, an ideally mixed annular flow with H/D constant was assumed since this is usually met in co-rotating twin screw extruders. This assumption guarantees an equivalent temperature development since the P and B numbers are held constant. Starting with the throughput desired and throughput obtained in the laboratory extruder, the diameter of the scaled up extruder was determined. Knowing the ratio of the diameters and using scaling powers for ideally mixed flow the power requirement was computed. These values were used to estimate the size of the equipment, energy requirements, inventory size. Table 8 shows a comparison of some of the important parameters in the lab scale and production scale extruders.

Equipment costs were obtained from Peters and Timmerhaus (Peters, 1991) using guidelines for solid-fluid machinery. Major equipment and material costs were obtained from manufacturers. Table 10 gives costs of the major pieces of equipment as shown in the PFD. Table 11 lists the break up of major components of investment. Equipment costs when necessary, were adjusted to 1998 dollars. Annual operating costs are estimated in table 12. Heat capacities were ob

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$$\frac{N}{N}$$

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$$\frac{P}{P}$$

$$\frac{Q}{Q}$$

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Fig

obtained from differential scanning calorimetry wherever required.

A product cost of \$2.63/Ib was estimated. This cost is higher than that of EPE alone. Further process optimization and the possibility of reduction in the cost of EPE will definitely push down the cost of the blend

$$\frac{N}{No}=\left(\frac{D}{Do}\right)^{n}$$

$$\frac{H}{Ho}=\left(\frac{D}{Do}\right)^{h}$$

$$\frac{L}{Lo}=\left(\frac{D}{Do}\right)^{l}$$

$$\frac{P}{Po}=\left(\frac{D}{Do}\right)^{p}$$

$$\frac{Q}{Qo}=\left(\frac{D}{Do}\right)^{q}$$

$$\frac{T}{To}=\left(\frac{D}{Do}\right)^{m}$$

Figure 30 - Some definitions of scaling powers for the mass and momentum equations

$$P = T2\pi N$$

$$Q = \frac{1}{2}V\cos\phi H\pi D\sin\phi$$

$$T = Ft\frac{1}{2}D$$

$$\dot{\gamma} = V\cos\phi / H$$

For laminar flow between parallel plates :

$$\text{Gz} = \text{Graetz number} = \frac{\text{convective heat transfer}}{\text{conductive heat transfer}} = \frac{\rho cVH}{\lambda}\frac{H}{L}$$

$$\text{Br} = \text{Brinkman number} = \frac{\text{viscous dissipation}}{\text{heat conduction}} = \frac{\mu V^2}{\lambda\Delta T}$$

For mixed annular flow :

$$\text{P number} = \frac{\textit{Peclet}}{\textit{Nusselt}} = \frac{\text{convective heat transfer}}{\text{radial heat transfer}}$$

$$\text{B number} = \frac{\text{Brinkman}}{\text{Nusselt}} = \frac{\text{viscous dissipation}}{\text{radial heat transfer}}$$

Figure 31 - Expressions for some of the relevant processing parameters and dimensionless numbers in continuous mixers

Throughput	$q = 2 + n + h$
Torque	$m = 3 + n + l - h$
Power	$po = 3 + 2n + l - h$
Shear rate	$g = n - h + 1$
Graetz	$gr = 1 + n + 2h - l$
Brinkman	$br = 2 + 2n$
P	$p = 1 + n + h - l$
B	$n = 2 + 2n - h$

Figure 32 - Some scaling Laws for throug put, mixing and dimensiole ss numbers

TABLE 7 - SOME OF THE SCALING POWERS OBTAINED FROM DIFFERENT SCALING STRATEGIES

Scaling Power	**Geometrical**	**Laminar**	**Ideally mixed L/D = const**	**Ideally mixed H/D = const**
Speed, n	0	-1	-2/3	**-1/2**
Channel depth,h	1	1/2	2/3	**1**
Length, l	1	1	1	**11/2**
Power, p	3	11/2	2	**21/2**
Torque, m	3	21/2	22/3	**3**
Throughput,q	3	11/2	2	**21/2**
Graetz, gr	2	0	2/3	**1**
Brinkman, br	2	0	2/3	**1**
P-number, p	1	-1/2	0	**0**
B-number, b	1	-1/2	0	**0**

TABLE 8 - LAB SCALE AND PRODUCTION SCALE VALUES OF SOME IMPORTANT PARAMETERS

PLASTICIZATION D/Do= 1.3864				
PARAMETER	**LAB SCALE**	**PRODUCTION SCALE**	**EXPONENT**	**UNITS**
Diameter	30	41.59	1	mm
Length	900	1,469.18	1.5	mm
Height	4.7	6.52	1	mm
Screw speed	125	106.16	-0.5	rpm
Torque	111.8	297.93	3	Nm
Power	1.23	2.78	2.5	KWH
Throughput	35	93.27	3	Ib/h
COMPOUNDING D/Do= 1.90468				
PARAMETER	**LAB SCALE**	**PRODUCTION SCALE**	**EXPONENT**	**UNITS**
Diameter	30	57.14	1	mm
Length	900	2,365.79	1.5	mm
Height	4.7	8.95	1	mm
Screw speed	125	90.57	-0.5	rpm
Torque	94.6	653.67	3	Nm
Power	1.46	7.31	2.5	KWH
Throughput	45	310.94	3	Ib/h

TABLE 9 - SCALEUP ASSUMPTIONS

Scaling strategy	Thermal - mixed annular flow H/D = constant
Production Ib/year	2500000
hrs/day	24
days/year	335
Depreciation	9%, straight line
Total federal taxes	34% of
Working capital	15% of total capital
Plant lifetime	10years
Base rate labor	$15/hr-person
Supervision	8% of fixed capital investment
Maintenance	7% of fixed capital investment
Local Taxes and Insurance	2%of fixed capital investment
R&D	5% of total manufacturing costs
Marketing	5%of total manufacturing costs
General, Sales, Admin	4%of total manufacturing costs
Utility costs	
Electric power $/KWH	0.07
Chilled water $/1000gallon	0.25
Purchased materials	$/Ib
Eastar Bio copolyester	2.15
Soy-concentrate	0.77
Glycerol	1
Material properties	Ib/ft3
Glycerol	75
soy-concentrate	30
EPE	75

q, the production exponent was assumed to be equal to 3 based on the manufacturers recommendation

TABLE 10 - EQUIPMENT COST BREAK UP

pfd code	**description**	**size**	**Purchase cost (1998$)**
	Core process machinery for mixing	**mm**	
E1	twin screw extruder	58mm	350000
E2	twin screw extruder	40mm	250000
		Subtotal	600000
	Storage	**Gallons**	
GLY	Storage - glycerol	972.7393	3100
SC	Storage - soy-concentrate	5662.51	12600
EPE	Storage - EPE	7506.177	13000
EPE:PSC	Storage - EPE:PSC	10723.11	13500
	all carbon steel	**Subtotal**	42200
	Feeding equipment	**Ib/h**	
PU	glycerol feeding pump	28.35	1000
F1	soy-concentrate feeder	66.15	5000
F2	EPE feeder	220.5	5000
		Subtotal	11000
	Downstream equipment		
B	Cooling bath	20 ft	2000
W	air wipe	12"	2000
P1	pelletizer	315Ib/h	5000
P2	pelletizer	94.5	5000
		Subtotal	14000
		Total	667200

TABLE 11 - INVESTMENT BREAK UP

Type of expense	**Percent of Purchased equipment cost**	**Actual cost**
Direct costs		
Purchase equipment		667,000
Purchase equipment installation	39	260130
Instrumentation and controls	13	86710
Piping (installed)	31	206770
Electrical (installed)	10	66700
Building (including services)	29	193430
Yard improvements	10	66700
Service facilities (installed)	55	366850
Land (if reqd.)	6	40020
		1,954,310
Indirect costs		
Engineering and supervision	32	213440
Construction expenses	34	226780
		440220
Total costs = Direct costs + Indirect costs		**2,394,530**
Contractor's fees(% direct cost)	5	119,727
Contingency (% of indirect costs	10	239453
Fixed capital investment		**2,753,710**
Working capital(15%total cap)		**485948.73**
Total capital investment		**3,239,658**

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TABLE 12 - ESTIMATION OF ANNUAL OPERATING COSTS FOR PLANT CAPACITY OF 2.5MILLION IBS

I MANUFACTURING EXPENSES				
	Unit	**unit/yr**	**$/unit**	**$/year**
A. VARIABLE COSTS				
1. RAW MATERIALS				
eastar bio copolyester	Lbs.	1750000	2.15	3762500
soy concentrate	Lbs.	525000	0.77	404250
glycerol	Lbs.	225000	1	225000
TOTAL RAW MATERIAL COST				4391750
2 UTILITIES				
electricity	kWh	86574	0.07	6060
chilled water	Gallon	66524	0.25	16
TOTAL UTILITY COST				6076
3. REGULATED COSTS				
operating labor - 2 operators * 24 hrs	Person hrs	15840	15	237600
supervision - 15% of operating labor				35640
maintenance and repairs (7% of Fixed Cap)				192759
Laboratory charges (10% of operating labor)				23760
general plant upkeep (60% of operating labor, supervision and maintenance)				279599
TOTAL REGULATED COSTS				769359
A. TOTAL VARIABLE COSTS = RAW MATL. + UTLITY + REGULATED				5167186
B. FIXED COSTS				
Depreciation (10%FCI)				275371
Local taxes & insurance (2.5% of FCI)				68842
B. TOTAL FIXED COSTS				**3442138**
I MANUFACTURING COST A+B				**5511400**

II GENERAL EXPENSES	
A. Administrative costs (15% of operating labor, supervision, maintenance)	69899
B. Distribution and selling (10% of total product cost)	655437
C. R&D (5 % of total product cost)	327718
II GENERAL EXPENSES A+B+C	**1053055**
TOTAL PRODUCT COST = MANUFACTURING COST + GENERAL EXPENSES	**6564455**
PRODUCT COST = ANNUAL OPERATING COST/ANNUAL PRODUCTION ($/lb)	**2.62**

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8. CONCLUSIONS AND RECOMMENDATIONS

A set of processing conditions was identified to attain an improvement in tensile strength of the EPE and soy protein blends. These conditions are briefly described below

- Soy concentrate gave better tensile properties compared to soy flour.

- Presence of glycerol was found to be necessary for obtaining an improvement in tensile properties, finely dispersed morphology and film formability of EPE:SC blends. The exact role of glycerol is unclear. A plasticizer usually leads to a reduction of mechanical properties. The improvement in mechanical indicates that there is a possibility of glycerol acting as a compatibilizing agent.

- It was not only essential to mix GLY with SC, but also it was found that subjecting the mixture to intense shear and heat in an extruder made significant difference in tensile properties. During plasticization a moderate to hi KB screw configuration was essential.

- Though compounding of EPE and PSC at 170C led to as fine a dispersion of PSC as at 135C, tensile properties of the blend prepared at 170C were lower than blends at 135C, when injection molded at 160C. Also miscibility based on the melting point depression was higher for blends compounded at 135C than for the 170C blends. Blends extruded at 135C and injection molded at 160C showed significant smearing of the PSC particles. The apparent contradiction of the melting point depression and tensile data with the morphology for blends extruded at 170 can be explained if degradation of soy protein is assumed. In all, compounding at temperatures around 135C with further processing such as injection molding at higher temperatures in the range of 160C yielded the best tensile strengths. A high KB screw resulted in good properties.

- Depression of the melting point with increase in the PSC content, the adhesion and smearing of particles seen in ESEM pictures indicate slight miscibility in the EPE:PSC blends

- DSC data reveals injection mold temperatures that can be used during cooling to maximize crystallinity and hence tensile strengths for different compositions. These temperatures can also be used for annealing of films.

- Replacement of GLY with ethylene glycol was not very effective. Low tensile properties and high torques during processing were observed.

- Use of compounded PSF yielded promising properties needing further investigation, as it can substantially reduce cost.

- Though repeatability testing could not be done, an improvement in tensile strength of films made for EPE:PSC::70:30 and EPE:PSC::80:20 blends over those of EPE alone was obtained. Further confirmation of this work would mean a postive deviation in the blend properties and thus compatibilization.

From the viewpoint of development of a commercializable application of the EPE - soy protein blends the following recommendations can be made

1. Reduce processing steps by combining plasticization and compounding in a single extruder. UNCMP PSC can be fed in the first zone, allowed to denature and then mixed with EPE introduced in the later zones.
2. Further optimize screw configuration between the moderate to high KB screws. Screws with even higher percent of kneading blocks than the high KB screw used in this work can be tried to see if any further improvement in properties can be obtained.
3. Increase gelation time between soy component and glycerol before extrusion. External heating of UNCMP PSC in other less expensive equipment with good uniformity in heating can be tried. This can reduce the cost of using the extruder during the plasticization phase.
4. Use temperature in the range of 135 - 140C for synthesis in an extruder and higher temperatures for further processing like - injection molding or film casting.
5. Work towards identification of film casting conditions for EPE:PSC::70:30 blend.
6. Develop a deeper understanding of the role of plasticizer in improving properties.
7. Minimize plasticizer requirement or use a cheaper plasticizer with suitable solubility parameter.

8. Address the bad odor problem encountered during processing.
9. Try using soy flour instead of soy concentrate to reduce costs
10. Check the possibility of using chemical analysis or selective extraction for verifying grafting.

APPENDIX A
FILM CAST LINE

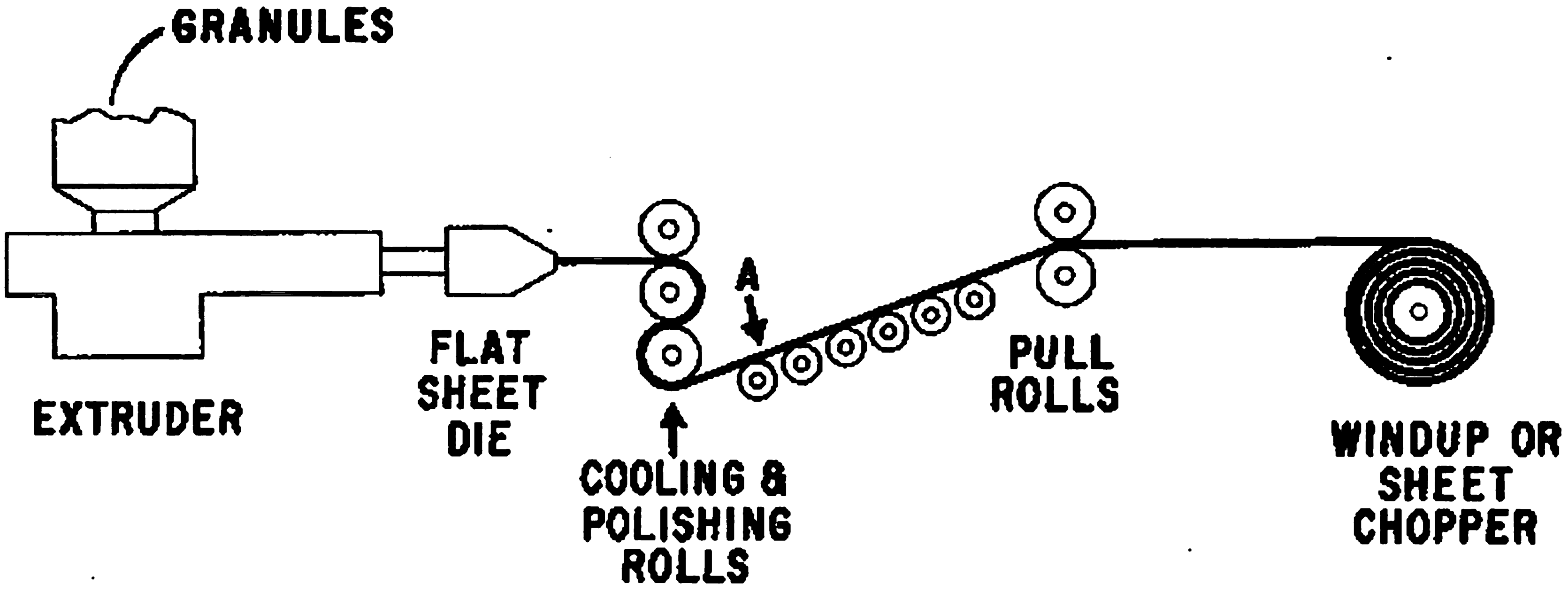

Figure 33 - Film cast line

APPENDIX B - SOY PROTIEN

Table 13 - Composition of soy flour and soy concentrate from Central Soya

	Soyafluff 200W	**Procon 2000**
Protein	52	70
Moisture	8.5	10
Crude fiber	4	4.5
Ash	7	
Fat	1.5	

Several different amino acids are found in proteins, which are covalantly attached through peptide bonds. Hence these materials are viewed as heterogeneous polymers. The composition of soy protein is given in table 14

Table 14 - Amino acid composition of soybean whole meal (Smith, 1972) [Grams of Amino Acid/16 Gm N]

Amino acid	**Weight**
Aliphatic amino acids with non polar R groups	
Alanine	4.51
Glycine	4.52
Leucine	7.72
Isoleucine	5.1
Valine	5.38
Hydroxyl amino acids	
Serine	5.57
Threonine	4.31
Sulphur amino acids	
Cystine	1.58
Methionine	1.56
Tyrosine	3.9
Tryptophan	1.28
Aromatic amino acids	
Phenylalanine	5.01
Acidic amino acids and amide derivatives	
Asparatic acid	12.01
Glutamic acid	21
Basic amino acids	
Lysine	6.86
Histidine	2.56
Arginine	8.42
Imino acids	
Proline	6.28

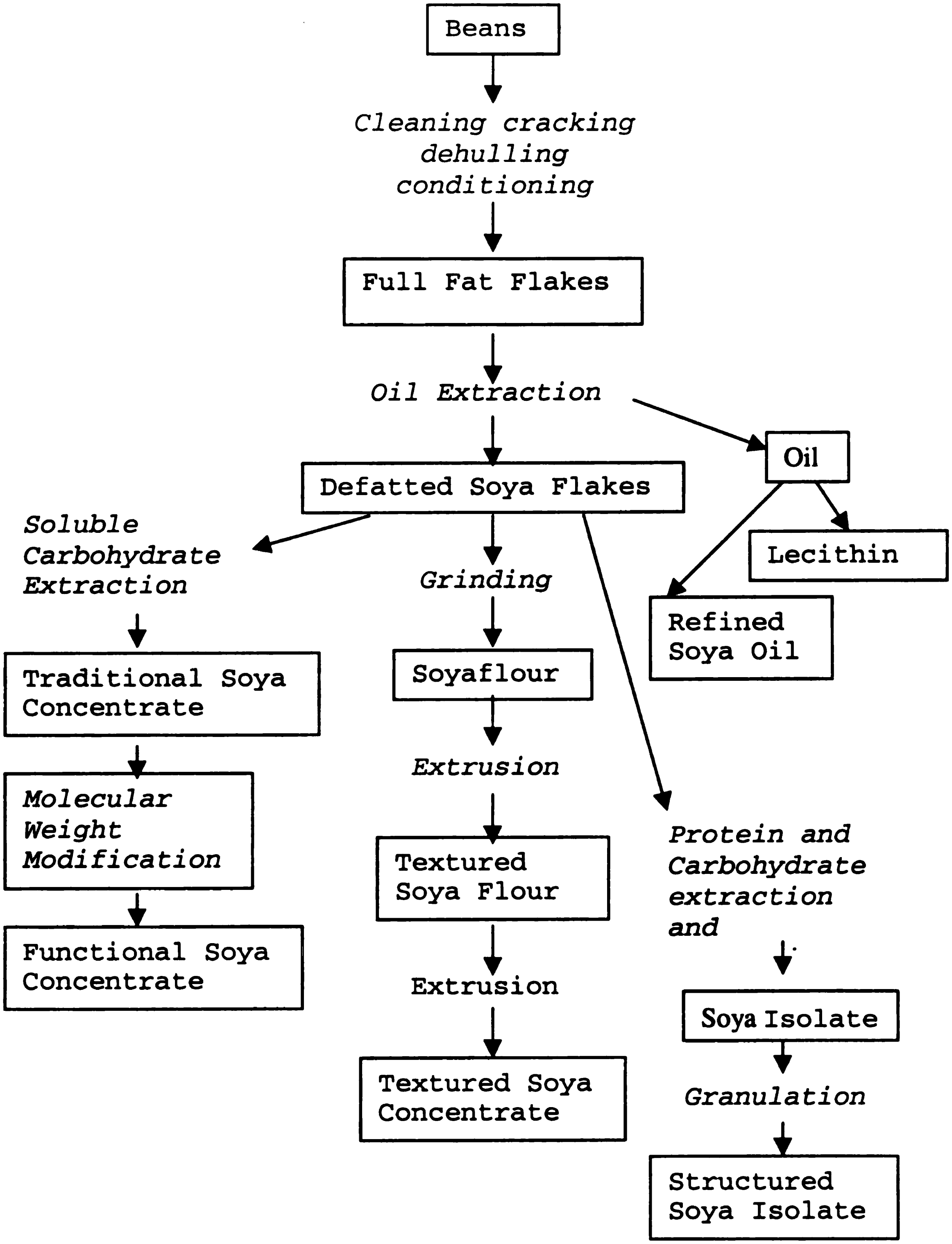

Figure 34 - Soy Protein Processing

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