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SURFACE SULFONATION OF POLYPROPYLENE RESIN TO IMPROVE THE MECHANICAL PROPERTIES OF WOOD FIBER/POLYPROPYLENE COMPOSITES

By

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ABSTRACT

SURFACE SULFONATION OF POLYPROPYLENE RESIN TO IMPROVE THE MECHANICAL PROPERTIES OF WOOD FIBER/POLYPROPYLENE COMPOSITES

By

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The effect of surface sulfonation on enhancing the mechanical properties of wood fiber/surface sulfonated polypropylene composites was investigated. The polypropylene (PP) resin in a powdered form was sulfonated for various reaction times (0, 5, 8, 10, and 20 minutes), and then utilized as a matrix phase in the fabricating composites with wood fibers (40% w/w). The mechanical properties of the respective composites, to include tensile properties, flexural properties, and Izod impact strength, were determined. The maximum sulfonation level achieved on the PP resin was considered low, resulting in a minimal enhancement in interfacial interaction between the wood fiber and the polymer matrix phase. While statistically significant enhancement in mechanical properties was observed with increased sulfonation levels, the results were not considered of commercial utility. No change in tensile strength of wood fiber/polypropylene composites was observed following storage up to 9 weeks at 35 ^{o}C and 90% RH, even though significant levels of water vapor were sorbed.

To my parents, Kongdej and Sompit

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INTRODUCTION

Composite materials are generally composed of one or more dispersed phases (reinforcing structure) enclosed in a continuous phase or matrix and are classified as particulate or fibrous, based on the geometry of the dispersed phase.

The type of reinforcing material is very important, since the properties of the composite are strongly related to the properties and quantities of the components, as well as their chemical and physical interactions. The reinforcing agent should provide maximum improvement of desired physical properties, be inexpensive and readily available, have good dispersion and wetting characteristics, and be available in controlled particle sizes, among other desired requirements.

Wood fibers, as a reinforcing filler for thermoplastic composites, have gained a significant amount of attention because of the many advantages they offer. Apart from their relatively low cost, such fillers have low density, low equipment abrasion, no health hazard, high strength-to-weight ratio and are easily renewable. The filler being investigated in this study, therefore, is Aspen Hardwood Fiber.

In considering polymer/wood fiber composites, the main drawback involves the hydrophilic character of the wood-

based filler surface, adversely affecting the interfacial interaction with the hydrophobic polymer phase.

To date, a number of studies have focused on the inclusion of dispersants and coupling agents with wood fiber/plastic composites, and the effectiveness of the additives in enhancing the interfacial interaction between the dispersed and matrix phases and thus, the mechanical properties of the composites. The polymer matrices investigated include: (i) high density polyethylene, (ii) polypropylene, and (iii) a recycled multi-layer polypropylene/adhesive/ethylene-vinyl alcohol copolymer container resin. The inclusion of modifiers in high density polyethylene based composites was found to enhance the mechanical properties of the resultant composites by improving fiber/polymer matrix adhesion (Selke et al., 1989 and Childress, 1991). Two additives which showed promising resultants were maleic anhydride modified polypropylene, and ionomer modified polyethylene. The multi-component composite (iii) was found to have properties superior to those of a composite formed with polypropylene alone (Simpson, 1991). This was thought to be due to improved fiber adhesion, resulting from the polar functionality of the adhesive and ethylene-vinyl alcohol copolymer components.

Sulfonation chemistry offers a new approach to chemically and structurally modifying the surface of polymers (Walles, 1989; Walles, 1973; and Walles, 1971). Since the sulfonation process introduces sulfonate groups along the polymer backbone, through a displacement reaction with hydrogen

atoms, virtually any polymer, except for fluoro-chloropolymers and some silicones, can be sulfonated. Further, the sulfonation process itself is not surface limited, i.e. the process can be extended under diffusion control below the surface up to depths of a micron or more. Thus, modification of not only the surface but the surface region is possible. In principle, this makes it possible to modify the surface of polymers, independent of their chemical composition, and can be applied to wood fiber/ polymer composites, resulting in enhanced compatibility and a concurrent improvement in adhesion and therefore mechanical properties.

Haraguchi (1993) evaluated the effect of surface sulfonation of high density polyethylene (HDPE) on the mechanical properties of HDPE/wood fiber composites, including tensile, flexural and impact properties. It was found that a longer exposure time in sulfonation of HDPE resin and an increased surface area of the resin (i.e. powder form) resulted in an increased level of sulfonation. The extent of sulfonation achieved, however, was quite low and did not modify the dispersive and polar characteristics of the polymer to a level which resulted in enhanced interfacial interaction between the HDPE and wood fiber with a concurrent increase in mechanical properties. Consequently, further studies were proposed by Haraguchi, designed to increase the sulfonation level of HDPE with a corresponding modification of surface energies of the polymeric matrix. In contrast to polyethylene, the sulfonation of polypropylene was found to readily modify the surface energy properties of the polymer

surface, since the presence of tertiary carbons on the polymer molecule provides active sites for SO_3 insertion (Wangwiwatsilp, 1993).

In the current study, surface sulfonation of polypropylene (PP) is being carried out in order to determine the effect of sulfonation on the chemical structure of the polymer surface region, and its effect on the mechanical properties of wood fiber/surface sulfonated PP composites. Therefore, the primary objectives of the study include:

1) Determination of the density and distribution of sulfonate groups on the surface of polypropylene following surface sulfonation.

2) Determination of the effect of sulfonate group concentration on the mechanical properties of wood fiber/ surface sulfonated polypropylene composites.

LITERATURE REVIEW

1. Composite Materials

1.1. Introduction

Several definitions of composites have been given in the literature. Since the term 'composite' refers to something made up of two or more distinct parts, a material having two or more distinct constituent materials or phases may be considered a composite material (Agarwal and Broutman, 1980). Composites may be separated into two basic forms, namely: (1) composite materials; and (2) composite structures. The latter are characterized by a discontinuous matrix, i.e. sandwich structures and coated materials, whereas composite materials are comprised of a dispersed filler embedded within a continuous matrix (Richardson, 1987). Furthermore, the composite concept can be related to either the microscale or macroscale (Richardson, 1977). The microscopic composite materials may not be generally regarded as composites in a strict application. In this study, a composite material has been defined as a macroscopic combination of two or more materials, as separate phases and combined to form desired structures so as to take advantage of certain desirable properties of each component (Grayson, 1983). For instance, fibers as a discontinuous phase are embedded within a continuous phase in fibrous composites.

Typically the discontinuous phase has higher strength and stiffness than the continuous (matrix) phase does. There generally must be a substantial volume fraction (~10% or more) of discontinuous phase (such as fibers) in order to provide reinforcement. The small cross sections potentially minimize flaws on the fiber structure, and thus fibers display much higher strength along their length than the bulk material. In order for fibers to be widely used for structural or nonstructural purposes and due to their small cross section, they need a binding material such as a matrix.

Two main functions of a matrix are: (1) to bind the reinforcements and hold them in place; and (2) to deform and distribute the stress to the fibrous constituents under an applied load (Schwartz, 1992). The matrix also serves to separate fibers from contacting each other. Since the fibers are likely to be brittle, the matrix additionally serves to protect the fiber surfaces against abrasion or environmental attack, both of which can lead to fracture. In composites, therefore, the strong and stiff reinforcing fibers contribute high tensile and flexural properties. On the other hand, the deformation of the matrix at crack tips absorbs energy and reduces stress concentration (Schwartz, 1992).

Composites can be classified into two groups: Particulate Composites and Fibrous Composites, based on the shape of the discontinuous phase (Agarwal and Broutman, 1980). Reinforcements in particulate composites are in the form of

'particles', which can be in various shapes, such as spheres, rods, flakes, and irregular shapes, with approximately equal dimensions. Fibrous composites, or so-called fiber-reinforced composites, are reinforced with the reinforcement fibers having a length much greater than their cross-sectional axes. Because of the shape of the reinforcing phase, fibers effectively improve fracture resistance of the matrix. In particulate composites, the particles are normally added for cost reduction, rather than for reinforcement, or they may be used for other purposes, such as for reducing shrinkage, for increasing surface hardness, etc. The relative hardness of the particles places constraints on the matrix deformation between the particles and the matrix, thereby improving the stiffness of the composites, but not potentially the strength (Agarwal and Broutman, 1980). On the other hand, composites with reinforcing fibers gain both strength and stiffness.

Two forms of the reinforcing fibers used for fibrous composites are continuous (or long) fibers and discontinuous (or short) fibers. Continuous-fiber composites, containing long fibers, are very strong in the direction of the fiber axis but are weak in the transverse direction. Continuous fibers bear stress equally at all points along their length and are primarily the load-bearing component in the load direction (Agarwal and Broutman, 1980). For short or discontinuous fiber composites, fibers are classified as having an aspect (length-to-diameter) ratio between 10-1000 (Richardson, 1977). Besides the fiber strength, the length of the fibers also greatly affects the mechanical properties

of the composites. Further, the transmission of stress imposed on the matrix to the fibers via interfacial interaction becomes crucial. If improved bonding at the interface is achieved, for a given system, the contribution of fibers to the composite mechanical properties can be maximized. Therefore, the properties of both the matrix and fibers, as well as the fiber-matrix interface, are very important to the composite properties.

1.2 Prediction of Properties

Theoretical models for predicting the mechanical properties of composites are useful and very convenient, where multiple variables, for instance, are studied and experimental approaches have limitations, i.e. time and cost. Nevertheless, in some cases, corrections for the derived equations are required because the models are based on various assumptions, all of which are rarely met in actual circumstances.

For simplicity, consider a composite system as having two components: a matrix material and continuous fibers that are uniformly dispersed in the matrix. It is assumed that there is a perfect interfacial bonding between the matrix and the fibers, so that both the matrix and fibers will deform equally under a longitudinal load applied to the composite system. According to the rule of mixtures, the tensile strength and modulus of composites can be estimated from equations (1.2.1) and (1.2.2):

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \qquad (1.2.1)$$

where: σ = tensile strength

V = volume fraction

in which subscripts c, f and m refer to the composite material, fiber and matrix, respectively

(Agarwal and Broutman, 1980).

It is generally assumed that the failure strain of fibers is less than that of a matrix. Under the longitudinal load, failure initiates when the fibers are strained to their fracture strain (Agarwal and Broutman, 1980). As the fiber elements run from end to end in the composite parts, the fiber strength is directly responsible for the strength of the composite.

$$E_c = E_f V_f + E_m V_m \qquad (1.2.2)$$

where: E = elastic modulus

(Agarwal and Broutman, 1980)

This equation indicates that under loading conditions, the load will be distributed over the matrix and fibers in proportion to their relative cross-sectional areas and elastic moduli (Richardson, 1977).

To be able to use high fiber strength proficiently, a larger ratio of fiber modulus to modulus of matrix should be obtained. This is because a higher proportion of the applied

load to the composite can be carried by the fiber phase. The increased volume fraction of fibers will improve the composite properties as well, but only within the scope in which the system can retain a very good bonding between the components (Agarwal and Broutman, 1980).

For some applications, it is advantageous to use short-fiber or discontinuous-reinforced composites, instead of continuous-reinforced composites. In this case, the strength of randomly discontinuous-fiber composites is equal in both longitudinal and transverse directions, and usually the short-fiber composites are produced by a cheaper and faster process. However, a sacrifice of a certain level of mechanical performance is inevitable. The elastic modulus of the randomly short-fiber composites, E_{random}, can be estimated using the empirical equation as shown by:

$$E_{\text{random}} = \frac{3}{8}E_L + \frac{5}{8}E_T \qquad (1.2.3)$$

where: E_L = longitudinal modulus

E_T = transverse modulus

(Agarwal and Broutman, 1980)

The longitudinal and transverse moduli must be obtained from the aligned, short-fiber composites having the same fiber aspect ratio and the same fiber volume fraction (Zadorecki et al., 1986). Both moduli of the aligned, short-fiber composites can be predicted from Halpin-Tsai equations, as shown by the following expressions. It is believed that the

predictions of these equations are quite accurate, unless the volume fraction of fibers is close to 1 (Agarwal and Broutman, 1980).

$$\frac{E_L}{E_m} = \frac{1+(2l/d)\eta_L V_f}{1-\eta_L V_f} \qquad (1.2.4)$$

$$\frac{E_T}{E_m} = \frac{1+2\eta_T V_f}{1-\eta_T V_f} \qquad (1.2.5)$$

where:

$$\eta_L = \frac{(E_f/E_m)-1}{(E_f/E_m)+2(l/d)} \qquad (1.2.6)$$

$$\eta_T = \frac{(E_f/E_m)-1}{(E_f/E_m)+2} \qquad (1.2.7)$$

(Agarwal and Broutman, 1980)

These Halpin-Tsai equations suggest that the aspect ratio (*l/d*) will have a significant effect on the longitudinal modulus, but not on the transverse modulus of the aligned, short-fiber composite. Further, it is predicted that the transverse modulus of either short-fiber composites or continuous-fiber composites is the same value. The moduli in both directions, however, are influenced by the fiber volume fraction and the modulus ratio of the fibers and the matrix (Agarwal and Broutman, 1980).

For composites, in addition to the matrix binding and holding the reinforcing fibers and protecting the fibers from handling and environmental hazards, the function of the matrix is also to convey the load to the fibers through the

from handling and environmental hazards, the function of the matrix is also to convey the load to the fibers through the fiber ends and small fiber length near the ends. In the case of long-fiber composites, the end effects can be neglected because of their much greater length over the length of which the fibers allow the transfer of stress. In contrast, for the short-fiber composites the end effects must be taken into consideration. The stress transfer for the short fibers is not uniform along the fiber length, in that the fiber ends insignificantly bear stresses, but the stresses acting on the fibers gradually build up while moving from the fiber ends, with the maximum value at the middle of fiber length. Concurrently, there is the variation of shear stress along the fiber length in the opposite manner (Richardson, 1977). The mechanism of stress transfer in composites can be understood by analyzing the force equilibrium of a small element of fiber as follows:

$$(\pi r^2)\sigma_f + (2\pi dz)\tau = (\pi r^2)(\sigma_f + d\sigma_f)$$

or

$$\frac{d\sigma_f}{dz} = \frac{2\tau}{r} \qquad (1.2.8)$$

where: σ_f = fiber stress in the axial direction

τ = interfacial shear stress on the cylindrical fiber-matrix interface

r = fiber radius

and dz = infinitesimal length of fiber

(Agarwal and Broutman, 1980)

The above relationship suggests that for a fiber of uniform radius, fiber stress will increase with the rate proportional to the interfacial shear stress. This can be integrated to obtain the fiber stress on a cross-sectional distance z away from the fiber end:

$$\sigma_f = \sigma_{fo} + \frac{2}{r}\int_0^z \tau \, dz \qquad (1.2.9)$$

where: σ_{fo} = stress on the fiber end

(Agarwal and Broutman, 1980)

Regarding the manner of stress distribution, load transfer from matrix to fiber will be attained only if the length of fibers is longer than a certain value, called a load-transfer length. The critical fiber length, l_c, considered to be the maximum value of load-transfer length, is the minimum fiber length in which the ultimate strength of fibers, σ_{fu}, can be achieved, and even the fiber over this length merely supports a stress up to the maximum fiber stress (Agarwal and Broutman, 1980). The critical fiber length can be given by:

$$\frac{l_c}{d} = \frac{\sigma_{fu}}{2\tau_y} \qquad (1.2.10)$$

where: τ_y = matrix yield stress in shear

$\frac{l}{d}$ = fiber aspect ratio

(Agarwal and Broutman, 1980)

The effect of the fiber ends is pronounced and becomes more important with a decrease in the fiber aspect ratio. The fiber reinforcing efficiency will be reduced as the length of fibers decreases. This is because a larger proportion of the total fiber length is not fully loaded (Hull, 1981).

Since the stress on the ends of the fibers is always under the maximum fiber stress, the average fiber stress at the critical length will be only $\sigma_{fu}/2$. This clearly shows that a much longer fiber length than the critical value will be needed in order for the load-bearing ability of the short-fiber composite to approach that of the continuous composites (Richardson, 1977). The end effects, therefore, result in the lowering of the elastic modulus and strength of short-fiber composites (Agarwal and Broutman, 1980).

In an estimate of the strength of aligned, short-fiber composites, the equation (1.2.1) must be modified. The average fiber stress will replace the tensile strength of the fiber. However, when the fiber length is longer than the critical length, the average fiber stress value becomes close to the maximum fiber stress (Agarwal and Broutman, 1980). The length of fibers in relation to the critical length can affect the fracture characteristics of the composites. The composite strength, as a function of the fiber length, is given as follows:

$$\sigma_{cu} = \frac{\tau_y l}{d} V_f + \sigma_{mu} V_m \ , \qquad l < l_c \qquad (1.2.11)$$

$$\sigma_{cu} = \sigma_{fu}(1 - \frac{l_c}{2l})V_f + \sigma_{mf}V_m \ , \quad l > l_c \qquad (1.2.12)$$

$$\sigma_{cu} = \sigma_{fu}V_f + \sigma_{mf}V_m \ , \quad l >> l_c \qquad (1.2.13)$$

where: σ_{cu} = composite ultimate strength

σ_{fu} = fiber ultimate strength

σ_{mu} = matrix ultimate strength

σ_{mf} = matrix stress at the fiber fracture strain

(Agarwal and Broutman, 1980)

These equations define three possible modes of failure, which affect the evaluation of the ultimate strength of short-fiber composites, depending on the fiber length. In the first case, when the fiber length is smaller than the critical length, the composite fracture is governed by the failure of the matrix or at the interface, even with the large size of the applied stress. This is because the maximum fiber stress is lower than the average fiber strength.

Secondly, when the fiber is longer than the critical length, the fibers may be loaded to their average strength. For this case, fiber failure will take place when the fiber stress is equal to the ultimate strength of the fibers. For the third case, where the fiber length is much greater than the critical length, the behavior of short-fiber composites becomes very similar to that of continuous-fiber composites (Agarwal and Broutman, 1980). In the last two cases, the

(Agarwal and Broutman, 1980). In the last two cases, the fibers are responsible for the failure of the composites. However, equations (1.2.12) and (1.2.13) are valid only if the volume fraction of fibers exceeds a certain minimum value. Otherwise the matrix, instead of the fibers, will support the entire load, even when all the fibers are broken.

The fiber ends may induce the building-up of stress. Even at a small load, the presence of stress buildup or stress concentration can result in the separation of fiber ends from the matrix, thereby producing a micro-crack in the matrix. One micro-crack at the fiber end may eventuate several adverse effects. By the propagation of the cracks along the fiber length, the shear stress at the interface may lead to fiber debonding and their separation from the remaining composite. In the other case, the micro-cracks near fiber ends could propagate in the cross direction to other fibers, resulting in immediate composite failure (Agarwal and Broutman, 1980).

During fabrication processes of composites, residual stresses may be inherently built up in the constituents and interface (Agarwal and Broutman, 1980), and the processing can induce fiber breakage (Bigg, 1985). Either residual stresses or fiber breakage will affect the composite strength.

Other parameters affecting the composites' mechanical properties include: (i) the strength of the matrix; (ii)

fiber orientation and distribution; and (iii) fiber-matrix interface bonding. The fiber orientation evidently influences the load distribution between fibers and matrix. The degree of off-axis fiber angle results in the reduction of the composite modulus, to some extent, and the tensile strength, to a greater extent (Lee, 1991). To maximize the mechanical properties, the fibers in composites must be parallel to the loading axis. In reality, it is very difficult to control the fiber alignments during fabricating composites, especially with high fiber loading of short fibers. The fibers should also be uniformly dispersed in the matrix. Poor fiber distribution may be a result of the close packing of fibers as well as the limitation of fiber wetting-out by the matrix. Furthermore, the incomplete wetting-out of fibers by the matrix or the presence of volatiles produced during the melt process can lead to the creation of void content (Hull, 1981). Less than 1 % voids is preferred in a good composite (Agarwal and Broutman, 1980).

The interfacial bonding between fiber and matrix phases is far more important to the behavior of short-fiber composites, compared to that of continuous-fiber composites. Since the fibers are not loaded directly under applied stresses, the stresses are transmitted from the matrix to the fibers through the interface, which contributes to a major portion of the composite strength. The stress transfer mechanism will be less efficient with poor interfacial bonding.

Moreover, the interfacial conditions govern the mode of micro-cracks at the fiber surface. The cracks do not propagate along the fiber length within a well-bonded system. The reinforcement efficiency still remains, even with several points of fiber breakage. Besides, a well-bonded interface is a prime factor in achieving the high transverse strength and good environmental performance of composites (Agarwal and Broutman, 1980). However, the enhancement of the composite modulus is much less influenced by the interfacial strength (Bigg et al., 1988; and Lee, 1991).

Concerning impact properties, there is no well-developed theoretical relationship for this prediction (Bigg et al., 1988 and Lee, 1991). Although the impact test is widely used as a means of measuring material toughness, the acquired numerical data are significant for qualitative analysis. For example, their use is in quality control, rather than in a quantitative way, such as the use in engineering design (Richardson, 1977). The major factors affecting the impact strength of the composite materials and unreinforced polymers are the testing procedure, rate of impact, shape of the impacting implement, degree and form of crystallinity, and the existence of microdefects in the vicinity of the impact. The impact strength is dependent on the fiber orientation, fiber aspect ratio and interfacial adhesion as well (Bigg et al., 1988).

1.3 Interface and Interphase

The interface is generally referred to as the interfacial region, or interphase, of the composite system, owing to the difference to some degree from its bulk properties. It is well-known that the characteristics of the interface play a key role in the mechanical performance of the composite materials. As aforementioned, the interface, which is responsible for the stress transmission from matrix to fibers, is a vital contributor to the composite properties.

In addition, the interfacial strength is essential for the enhanced environmental performance of the composite. The strength of interfacial bonds must be at least equivalent to that of the matrix, particularly under loading conditions. Otherwise, composite failure such as fracture and delamination at the interface will take place. The quality of the bond is also responsible for the long-term stability of the composite, such as fatigue properties and resistance to hot-wet conditions (Schwartz, 1992).

In the combination of two dissimilar components, the degree of interfacial adhesion between the composite elements may differ from strong chemical bonding to weak frictional forces. This is a design variable which can be regulated by utilizing one or more of the following techniques: 1) modification of fiber; 2) modification of matrix; and 3) inclusion of interfacial-aided additives (Krishnan and Narayan, 1992).

There are five possible mechanisms of adhesion which can occur, either by themselves or in combination, at the fiber-matrix interface of a composite material: (1) mechanical adhesion, (2) adsorption and wetting, (3) interdiffusion, (4) electrostatic attraction, and (5) chemical bonding (Hull, 1981).

(1) Mechanical Adhesion. The intimate contact of two surfaces results in a mechanical interlocking between the two surfaces. For good mechanical adhesion it is necessary that a molten resin thoroughly wets a rugged fiber surface. The degree of surface irregularity will affect the strength at the interface, since these contact areas increase as the extent of irregular surfaces into which the liquid can penetrate, increases.

(2) Adsorption and wetting. A physical attraction, i.e. Van der Waals forces, occurs as a result of the wetting of every pore of solid surfaces by liquids. Strong bonds can be achieved if the entrapped air/ gases or impurities at the fiber surface are avoided.

(3) Interdiffusion. A bond is formed between two surfaces by molecular entanglement. The presence of solvents and plasticizers can promote the bonding, while the extent of diffusion and the number of molecules involved will designate the strength of the bond.

(4) Electrostatic attraction. The electrostatic forces, i.e. ionic bonding, take place when the contact is presented

between two surfaces carrying oppositely charged ions. The strength of the bonds is governed by the charge density. This attraction may aid in the coupling effect, but it is unlikely to be a major contribution to the bond strength of the composite materials.

(5) Chemical Bonding. A chemical bond is formed across the interface as a result of the presence of compatible chemical groups on the fiber surface and the matrix surface. The use of coupling agents on glass fibers is one of the examples of reliance on this mechanism.

2. Sulfonation

2.1 Introduction

The surface composition of polymers can be chemically or mechanically modified to provide new properties, such as surface adhesion, wettability and printability, for the respective polymers. Among various techniques for surface modification, sulfonation provides a series of desirable characteristics, especially being a well-controlled, reproducible process, that is attractive either to laboratory research or to industrial practice (Asthana, 1993).

It has been reported that the sulfonation process creates sulfonates, by introducing polar groups of sulfonic acid on the polymer backbone, with carbon-sulfur bonding between them. Sulfonating reagents in use include, sulfur trioxide (SO_3) in the form of gas and liquid, as well as a variety of SO_3 complexes, (i.e. pyridine, trimethylamine, trioxane, dioxane, trialkylphosphate) and oleum. Oleum, or fuming sulfuric acid, is among the most popular reagents in commercial use (Gilbert, 1965).

Typically, a sulfonated substrate can be any polymer containing either carbon-hydrogen bonds or nitrogen-hydrogen bonds, with exception of pure fluorocarbons and some silicones (Walles, 1989). Thus, the common engineering polymers such as polyethylene and polypropylene, having low surface energy or non-polar nature, can be treated via a sulfonation process for tailored surface properties. The surface layer of a sulfonated polymer substrate is modified

to behave differently from its bulk composition due to the presence of sulfonate groups. This modification results in observed changes in surface properties.

Surface sulfonation of polymers has shown its utility in enhancing several surface physicochemical properties, such as adhesion, wettability, barrier properties, dyeability, abrasion resistance, electrical conductance and metallization (Erickson, 1993). For example, the organic vapor permeability of fuel tanks can be considerably reduced by exposing the inner surface of the containers to SO_3 gas under controlled conditions, with subsequent neutralization with NH_3 gas (Walles, 1989). The findings from Wangwiwatsilp (1993) also showed a reduction in the permeability coeffiecient of ethyl acetate and toluene through sulfonated polypropylene films. It was reported by Park (1993) that the surface sulfonation afforded an increase in the polar component of the surface energy and the peel adhesion strength of a polypropylene film.

In addition, the study of Fonseda et al.(1985) indicated that the direct sulfonation of polyethylene successfully increased the surface conductivity, the microindentation hardness and the critical surface tension of this polymer. The reported applications of the sulfonation process are at the manufacturing level, including the manufacture of detergents (surface active agent), dye intermediates, ion-exchange resins, sulfonated oils, and other sulfonates of industrial interest (Gilbert, 1965).

Although most of the reaction occurs on the polymer surface, sulfonation could extend beyond the surface to the bulk thickness. Walles (1989) indicated that when NH_3 gas was used in the neutralization step following the SO_3 gas phase sulfonation, the penetration of sulfonate (i.e.-$SO_3^-NH_4^+$) groups was found to a depth of 20-25 micrometers. Further, it was found that the extent of sulfonation, as well as the depth of surface modification achieved, is apt to be manipulated by the concentration of SO_3 and time of exposure. These two sulfonating parameters are inversely related to each other, so that their combination can be varied to suit a specific purpose (Walles, 1973).

2.2 Sulfonation Reactions

Sulfur trioxide has an amphoteric characteristic due to the strongly electron hydrophilic nature of the sulfur atom and the electron-rich nature of the oxygen atom. This amphoteric character explains its behavior as a sulfonating agent, with the atomic sulfur attacking electron-rich (basic) systems, and the atomic oxygen accepting acidic protons.

The nature of the sulfonation process is fairly complicated, with a number of studies reported in the literature to elucidate the mechanism of polymer sulfonation. Olsen and Osteraas (1969) studied sulfonated polyethylene (PE) surfaces employing an infrared spectrophotometric technique. The results confirmed the insertion of atomic sulfur on the polyethylene surface, as the presence of sulfonic acid groups on the PE surface was found following sulfonation. It was reported by Walles (1973), that virtually all sulfur

atoms were in the form -C-SO_3H (alkane sulfonic acid) groups, with much less degree of -C-O-SO_3H (hydrogen sulfate) for the sulfonated PE structure.

In the study of Ihata (1988), the spectra obtained by infrared, resonance Raman and UV-VIS spectroscopy showed the formation of sulfonic acid functionality during the sulfonation reaction, in accordance with other research. Further, this investigation revealed the possible sulfonation mechanism of polyethylene with gaseous SO_3 as shown in Figure 1. Firstly, a hydrogen atom on the polymer chain is removed by SO_3 to give a PE radical. The subsequent mechanism could be either the reaction of PE molecular species with SO_3 to form sulfonic acid groups, or the removal of sulfurous acid to generate polyene. As the reaction proceeds, longer conjugated polymer chains with sulfonic acid functionality were formed.

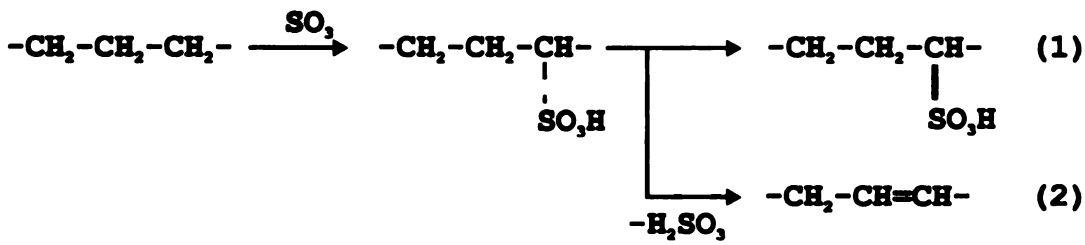

Figure 1: Sulfonation reaction of PE (Ihata, 1988)

In addition, a color change of PE was found as a result of the sulfonation process. Color varied from pale green to dark brown, as the extent of sulfonation increased. A similar result of color change on PE surfaces was reported by Walles (1973) who proposed that the color was induced by various substances resulting from oxidation reactions occurring during the surface modification.

For the sulfonation of polypropylene, Asthana (1993) proposed that, like polyethylene, the reaction mechanism involved the insertion of SO_3 at active sites to yield sulfonic acid functionality, which was followed by the elimination of sulfurous acid groups. Regarding the polypropylene structure, the tertiary carbon atoms of the polymer are considered as tentative active sites for SO_3 insertion, owing to their high electron density, which would be favored by the hydrophilic reaction with SO_3. The resulting sulfonic acid groups, however, are likely to desulfonate by the removal of sulfurous acid. The sulfonation reaction of polypropylene is shown in Figure 2. The desulfonation reaction may continue yielding a final product, or intermediates of desulfonation may pursue new reactions. Consequently, it is a complex reaction and various products can be produced, i.e. alkene sulfonic acid, C-sultone, D-sultone, ketones, etc., during the reaction (Asthana, 1993).

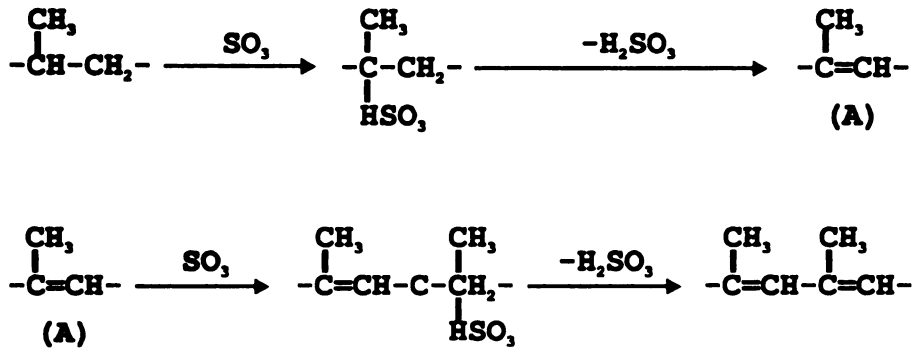

Figure 2: Sulfonation reaction of PP (Asthana, 1993)

Following sulfonation, it is essential that the SO_3 groups on the polymer skeleton are neutralized to form a stable species. A variety of neutralizing agents can be used, including aqueous ammonium hydroxide (NH_4OH), ammonia gas (NH_3), sodium hydroxide (NaOH), etc. If NH_4OH is utilized, the hydrogen atom of the sulfonic group will be substituted by a NH_4^+ ion ($-C-SO_3^-NH_4^+$) which is a more stable form. Certain properties, such as barrier properties, can be tailored through the selection of neutralizing agent. This is the result of the nature of the counterion influencing the barrier properties of the sulfonated layer. For example, a substantial decrease in oxygen permeability of sulfonated HDPE was achieved after the cationic exchange of NH_4^+ to Lithium (Li^+) or Sodium (Na^+) ion. Among common metal cations, Li, Na, Cu, Mg, Sr, V, Mn, Co, and Ni can give effective barrier results (Walles, 1989).

3. Review of Prior Research

A number of literature references have focused on the fabrication and properties of cellulose-based composites, particularly with polyolefins. Specific attention has been directed to developing techniques for the improvement of cellulosic composite performance, due to its clear opportunity in competition with other composites, i.e. glass fiber-thermoplastic composites. The following is a review of prior research related to this field.

Klason, Kubat and Stromvall (1984) studied the efficiency of cellulosic fillers in common thermoplastics, which included high density polyethylene (HDPE), polypropylene (PP), normal and impacted-modified polystyrene (PS, SB), and polyamide 6 and 12 (PA6, PA12). The fillers used were wood flour (white spruce), cellulose flour (bleached sulphate, pine) and cellulose fiber (bleached sulphate, birch). Overall, the modulus was improved with increased filler content, whereas the strain at yield and at rupture, and the charpy impact resistance diminished substantially. The tensile stress at yield and at break of HDPE and SB composites were increased to some extent, whereas the others were relatively unaffected. The polyamide and polystyrene composites exhibited unfavorable characteristics, i.e. degradation and discoloration, when being processed. Only polyolefin composites were able to achieve 70% filler content. Two compounding procedures were evaluated, the first by using a kneader, and the second involved a single-screw extruder. The kneader compounding process provided for better homogeneity, and, therefore, higher impact strength

resulted. The dimensional stability was also investigated. Of the filled polymers, a decrease in mold shrinkage was displayed, with an increase of filler content. As a filler, cellulose fibers did not exhibit a significant contribution in reinforcement of the resultant composites, despite their strength potential. This was attributed to fiber breakage during the fabrication step and poor adhesion at the polymer-wood fiber interface.

Using a compatibilizer to promote the interfacial adhesion in biofiber-polypropylene composites and its effect on mechanical properties were investigated by Krishnan and Narayan (1992). They used low-density hardwood residue mixed with ground pecan shells (LDHW) as a biobased component for the composites. Two fiber-content levels of 20% and 30% were fabricated. The compatibilizer employed was the graft copolymer of maleated polypropylene with cellulosic parts. Two different processes used in modification were A- and B-modified processes. In the A-modified process, the blend of polypropylene (PP), maleic anhydride (MA) and dicummyl peroxide (DCP) was extruded and pelletized, to produce maleated polypropylene (MAPP). Then, MAPP, maleic anhydride and LDHW were compounded in the presence of the catalyst. For the B-process, a single run of the PP, maleic anhydride, dicummyl peroxide, LDHW and the catalyst was produced. Both blends with compatibilization showed improved tensile properties over the unmodified composites. Yet, in contrast to composites fabricated by the A-process, the B-modified materials exhibited a lower percent elongation than the virgin polymer. This was thought to be due to crosslink

formation by simultaneous reaction of the maleic anhydride with lignocellulosic polymer and polypropylene.

Raj and Kokta (1991) examined the use of silane coupling in silane-coated wood fiber/linear low density polyethylene (LLDPE) composites. Three silane coupling agents used were vinyltri(2-methoxy ethoxy)silane (silane A-172), γ-methacryloxypropyltrimethoxysilane (silane A-174), and γ-aminopropyltriethoxysilane (silane A-1100). The wood fibers were coated with the different coupling agents before mixing with LLDPE. Loss of tensile strength and increase of modulus were found in the composite having untreated wood fiber, with an increase of filler concentration. On the other hand, the use of both silane A-172 and A-174 resulted in a considerable increase in the mechanical properties of the resultant composites, as compared to the untreated wood fiber composites. The tensile strength was increased with the addition of filler content. The effectiveness of the silane coupling agents to improve bonding at the fiber-polymer interface was evident even at low concentration (<2% by weight of fiber). The authors also indicated the significance in the choice of an initiator (peroxide), which can aid in chemical bond formation between the cellulosic polymer and the coupling agents. The morphology of the polymer-wood fiber composites, as indicated by scanning electron microscopy (SEM), confirmed the above results, where poor dispersion and adhesion of wood fiber with the matrix in the untreated fiber composites, and good bonding at fiber-matrix interface in the pretreated wood composites were shown. Among the three coupling agents evaluated in

this study, the silane A-174 performed the best, followed by the silane A-172. This was attributed to their respective functional groups.

Raj, Kokta and Daneault (1989) reviewed the effect of fiber treatment on mechanical properties of polypropylene-wood fiber composites. Two commercial pulps (Tempure 626 and Temalfa-A 6816), and chemithermomechanical aspen were used as reinforcing agents. Various treatments were applied to the fibers. Composites of the fibers with pretreated silane coupling agents (Silane A-172 and A-174) produced decreased tensile strength and elongation. Unlike silane treated composites, the fiber coated with maleated polypropylene, polymethylene polyphenylene isocyanate (PMPPIC) and polypropylene combination gave better tensile strength and modulus with an increased fiber level (0 to 40%). This was attributed to the reactivity of isocyanate with wood fibers in the coated fiber composites. In this study, there was no substantial effect of the initiators, dicummyl peroxide or cummine hydroperoxide (2%), in promoting bonds at the fiber-matrix interface. It was also found that the shorter fibers with 60-mesh size favorably compared to 20-mesh fibers in the coated fiber composites.

Gatenholm et al.(1992) also described studies involving cellulose fiber/polymer composites. The authors found that with an increased fiber loading, the use of maleic anhydride-modified polypropylene (MAPP) as a coupling agent in cellulose-polypropylene composites influenced dramatically an improvement in the material strength. A

measurable increase in the ductility was also reported. Different degrees of adhesion in composites were exhibited by the fracture surface images. The outcome from FTIR also revealed the presence of bonding between cellulose and MAPP. Studies involving varying the molecular weight of the coupling agent indicated that the greater the molecular weight of MAPP, the better interfacial adhesion, or the higher tensile strength of the composites. In addition, a prehydrolytic treatment of fibers, resulting in reduction of fiber size, was presented to promote processability and homogeneity of the composite. Lastly, Gatenholm et al. (1992) proposed the use of polyhydroxylbutyrate (PHB) in cellulose composites as a biodegradable composite having good mechanical properties.

The structure-property relationships of polypropylene/wood fiber composites were studied by Sain, Kokta and Imbert (1994). Three types of wood fibers were evaluated, including: (i) chemithermomechanical pulp (CTMP); (ii) sawdust; and (iii) explosion pulp. The mechanical and thermal properties, in relation to the morphological structure, were investigated in unmodified and modified composites. The interface modifiers, including maleic anhydride, itaconic anhydride and m-phenylene bismaleimide, were pretreated on PP, and m-phenylene bismaleimide was pretreated on CTMP. The cause of deterioration of mechanical properties with higher fiber loading was indicated by the morphology of the respective composites. Phase separation of fiber and matrix with fiber agglomeration in highly fiber filled, unmodified composites indicated poor dispersion and

the presence of micropores. Treatments of maleated PP (MPP), itaconic anhydride modified PP (ITPP), and bismaleimide modified CTMP (BCTMP) were found to improve the mechanical properties, such as strength and toughness of the wood-PP mixture, as compared to those of unmodified composites and unfilled PP. The modified mixtures also exhibited better thermal properties (i.e. decomposition temperature and melting point) and more uniformity in structure over the unmodified counterparts. This was thought to be due to lowering of the interfacial surface energy with the use of modifiers.

Recycled polyolefins (95% PE and 5% PP) utilized as a matrix in wood filled composites, were considered by Chtourou, Riedl and Ait-Kadi (1992). The wood fibers in the form of chemithermomechanical pulp (CTMP) consisted of 45% Spruce, 45% Fir and 10% Poplar. The compounding materials were formed by compression and injection molding. Tensile strength at yield and modulus of the composites showed improvement as a function of non-treated fiber content (0 to 30%). The properties of unmodified composites at 10% weight of fiber were compared to those of the acetic anhydride (AA) and phenol-formaldehyde (PF) treated fiber composites, of the same fiber loading. The authors concluded that both fiber treatments generally increased tensile properties, particularly the modulus of the respective composites. This was attributed to the improved interfacial interaction by the treatment of AA or PF. The extent of the treatment was also of interest. The greatest enhancement of the properties was found at about 12% AA content (or at 12% PF). Both

treatments in compression molding gave more favorable properties as compared to those of the same treatments in injection molding, due to higher deformation rates of fibers in injection molding. Furthermore, samples stored under humidified conditions showed less water uptake and relatively high tensile properties for the treated fiber composites, in comparison with the nontreated composite structures.

The effect of extreme storage conditions on the mechanical properties of linear low density polyethylene composites was investigated by Kokta, Daneault and Beshay (1986). The fillers employed in the composites included: (i) grafted chemithermomechanical pulp (CTMP) of aspen; (ii) wood flour; (iii) mica; and (iv) glass fiber. Their mechanical properties, including: absorbed energy (area under stress-strain curve), secant modulus, tensile strength and strain at yield were measured. The four different storage conditions were (1) room temperature; (2) boiling water; (3) 105 °C ; and (4) -40 °C. The mechanical properties of the grafted aspen fiber-filled composites remained relatively unaffected after being exposed to extreme conditions, except for the modulus, tensile strength and strain when measured at -40 °C condition. Overall, grafted CTMP improved polyethylene properties and gave superior mechanical properties to either mica or glass fiber based composites. With respect to water uptake by the composite samples following four-hour immersion in boiling water, the investigators found increased water uptake at higher fiber loading for composites of treated pulp. The treated pulp

composite also exhibited better dimensional stability than those of mica or glass fiber filled composites.

The analysis of tensile and impact properties of recycled newspaper fiber-filled polypropylene composites was reported by Sanadi et al.(1994). Coupling agents incorporated in the composite system were (i) E-43 : maleic anhydride-grafted PP (MAPP) with MW = 10,000 and 6% maleic anhydride (MA); (ii) G-3002 : MAPP with MW = 40,000 and 6% MA; (iii) BPMA : MAPP with MW $\geq$ 100,000 and <0.5% MA; and (iv) AABP : acrylic acid-grafted PP with 6% acrylic acid (AA). Two mixing methods were evaluated which were described as the single stage and two stage methods. The two stage technique, where PP was added later to the mixture of the fibers and coupling agent, exhibited slight improvement in tensile and unnotched impact strength over the properties of samples from the single stage method. An increase in tensile strength was found for the E-43 and G-3002 composites, whereas there were modest increases by BPMA and smaller improvement in the AABP systems, when compared to that of the uncoupled specimens. The level of molecular weight and graft content for MA were found to be the main factors contributing to the mechanical properties of the composites. The unnotched impact strength was improved with inclusion of coupling agents. The values of strengthening efficiencies were still fairly low for the well bonded composites. This was believed to be due to the short fiber lengths in the system.

Childress (1991) investigated the effect of additives on mechanical properties of wood-fiber/high density

polyethylene composites. The additives used were maleic anhydride modified polypropylene (MAPP) at 1, 3 and 5% weight ratios; ionomer modified polyethylene (Surlyn) at 1, 3 and 5% (wt/wt); and two low molecular weight polypropylene resins (Proflow 1000 and Proflow 3000), each at 5% (wt/wt) loading. The properties evaluated included tensile properties, impact strength, creep and water sorption. Only MAPP functioned as a true coupling agents which enhanced composite properties overall. Generally, Proflow 1000 and 3000 decreased the mechanical properties of the respective composites. Surlyn exhibited a small effect on tensile properties. Water sorption was likely promoted by Surlyn and Proflow 3000. However, the results showed no significant difference from the composites without additives.

Simpson (1991) studied the use of recycled multi-layer polypropylene bottle resin with wood fiber in the form of composites. In these studies, 30, 40 and 50% (wt/wt) of fiber content were incorporated into composites of virgin PP and PP Reclaim (PPR). For comparison, samples from the original polymers were produced. Tests were performed to evaluate the tensile properties, flexural modulus, impact strength, creep and water absorption, all in lengthwise and crosswise fiber directions, except for the creep and water absorption tests. The structure of the PP Reclaim was PP/adhesive/EVOH/adhesive/regrind/PP. In general, the test results were favorable in the lengthwise direction. Simpson (1991) concluded that higher mechanical properties were exhibited by PPR-wood fiber composites, as compared to PP-wood fiber composites. Also, the PPR composites afforded

longer retention under load values, either at ambient or extreme conditions. This was thought to be the result of contributions of the components in the PP Reclaim structure to interfacial bonding. In addition, an increase in water absorption was found with an increased fiber concentration.

MATERIALS AND METHODS

1. Materials

1.1 Matrix

The polymer used as a matrix for all composites was the injection molding grade of polypropylene homopolymer (Profax 6501) in a powdered form, which was supplied by Montell U.S.A., Inc., Lansing, Michigan. The reported properties of the polypropylene (PP) are shown in Table 1. The melting point and percent initial crystallinity of the resin were measured by a DSC 2920 Modulated Differential Scanning Calorimetry (MDSC), manufactured by TA Instruments, New Castle, Delaware. The values are 164.2 ^{o}C and 34% respectively. The heat transition curves from MDSC are shown in Appendix A.

The surface area of the polymer determined by Nitrogen Adsorption at -196 ^{o}C using a Micromeritics Pulse Chemisorb Model 2700 apparatus is approximately 0.09 m^2/g. The particle sizes of the resin were determined by the sieve mesh technique. Over 90% of the PP particle sizes were found in the range of 355 to 855 microns. The moisture content of the powdered PP resin is 0.08%.

Polypropylene is a linear thermoplastic having propylene monomers as building blocks. The repeating monomer unit of PP structure is shown in Figure 3. Three different types of

stereochemical configurations are isotactic, syndiotactic and atactic, depending on the catalyst and process of polymerization. The most commonly used form of PP structure is isotactic (Modern Plastics), which is the highest regular form of PP and is a crystalline polymer. Due to its methyl pendant groups, PP has a relatively high glass transition temperature (Tg) and high melting point (Tm), so that PP is stiffer and stronger but lower in percent crystallinity and ductility, if compared to polyethylene. PP has excellent chemical resistance with the exception of strong oxidizers and nonpolar solvents. It is also highly resistant to moisture (hydrophobic). The low surface energy results in very low bonding, printing and painting ability. In addition, PP is susceptible to sunlight and heat by an oxidative degradation process (Seymour and Carraher, 1984).

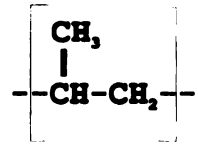

Figure 3: Repeating unit of PP Structure

Table 1: General Properties of Pro-fax 6501 (Source: Montell U.S.A., Inc.)

Properties	Averaged Value
Melt flow rate, dg/min	4
Density, g/cm^3	0.9
Tensile strength at yield, MPa	35
Elongation at yield, %	12
Flexural modulus, MPa	1700
Notched Izod impact strength, J/m	
at 23 °C	40
at -18 °C	<16

1.2 Reinforcing Filler

Aspen hardwood fibers in the form of thermomechanical pulp were utilized as a reinforcing filler for all composites in this study. The fibers were obtained from two sources: (1) Canfor Panel and Fibre Division (New Westmister, B.C., Canada); and (2) Georgia-Pacific Corporation (Phillips, Wisconsin). The fibers from sources 1 and 2 will be referred to Fiber-1 and Fiber-2 later in this study.

Wood is a natural polymeric, cellular structure with hydrophilic and polar functionality. Three basic organic constituents of wood are cellulose, hemicellulose and lignin. In general, hardwoods are composed of 41-45 % cellulose, 23-30 % hemicelluloses and 19-28 % lignin by weight (Mullins and McKnight, 1981). The dimensions of

hardwood fibers range from 1.0 to 1.5 mm. in length and average 15 microns in diameter (Stamn, 1964).

Cellulose $(C_6H_{10}O_5)_n$ is a linear chain structure composed of β-D-glucopyranose units with a 1,4- glucosidic linkage (Browning, 1963). The cellulose molecule is illustrated in Figure 4. This macromolecule contains monomer units ranging from 8,000 to 10,000, on average (Dinwoodie, 1989). Cellulose consists of crystalline and amorphous domains. Up to 70% of cellulose is crystallites. Intermolecular and intramolecular bonding of cellulose molecules in crystalline regions is very strong, which makes it hardly accessible to chemical reaction (Mullins and McKnight, 1981). The amorphous regions are permeable so that the hydroxyl groups are readily attacked by reactant molecules such as water.

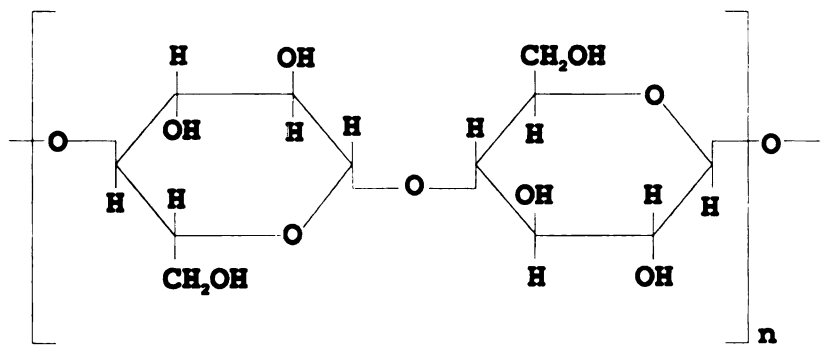

Figure 4: Cellulose Molecule

Hemicelluloses are polysaccharides made of various sugars including glucose, galactose, mannose, xylose and arabinose. The hemicellulose molecules are more complex and lower in molecular weight than the cellulose. Hardwood hemicelluloses have a large proportion of xylan. Glucomannan, consisting of glucose and mannan units, is at a level of 3-5 % in hardwood. Hardwood xylan is comprised of a series of xylose units linked end to end as a backbone. Methyglucoronic acid groups and acetyl groups are attached to the backbone, with ratios of 1 and 7 units, respectively, for every 10 xylose units (Mullins and McKnight, 1981).

Lignin is an amorphous polymer composed of hydroxyl- and methoxy-substituted phenyl propane units. It, as the structural support and cement material of plants, is concentrated in the spaces between wood cells and deposited within the matrix of cellulose microfibrils. Lignin in hardwood contains guaiacyl (coniferyl alcohol) and syringyl alcohol units formed as a copolymer of the two alcohols (Dinwoodie, 1989).

2. Methods

2.1 Sulfonation Treatment

Sulfonation treatment of PP resin was performed at the Composite Materials and Structures Center (CMSC), Michigan State University. The sulfonation system unit was designed and manufactured by Coalition Technologies, Ltd. (Midland, Michigan). The principal operational components for the sulfonation process include a Sulfur Trioxide Generator and a Rotating Drum Reactor. The sulfur trioxide (SO_3) gas was

generated in the Generator. The rotating drum reactor is the chamber where the polymer substrate is held and the reaction of SO_3 on the polymer surface takes place. A schematic diagram of the Sulfonation System is illustrated in Figure 4. The operating cycle of the sulfonation process is briefly described below.

First, an amount (~1816 grams) of powdered PP resin was charged into the rotating drum reactor and the connection between the generator and the rotating drum was made. Nitrogen (N_2) was purged through the chamber for 10 min at a flow rate of 120 cc/min, then a vacuum (10^{-1} to 10^{-2} torr) was applied for 5 min, and N_2 was purged through the rotating drum reactor again for 5 min. Water and other reactants were eliminated or minimized in this step before introducing gaseous SO_3 to the chamber. A flow of SO_3 gas at a concentration of 0.7% (v/v) was forced continuously through the reactor for a period of time (5, 8, 10 and 20 min). Following the indicated reaction time, N_2 was purged through the reactor for 10 min to remove residual SO_3 gas. The neutralization process was started by introducing ammonia gas (NH_3) for 1-2 seconds. The drum reactor was rotated for a few minutes, and the process was ended by purging N_2 through the reactor for 5 min.

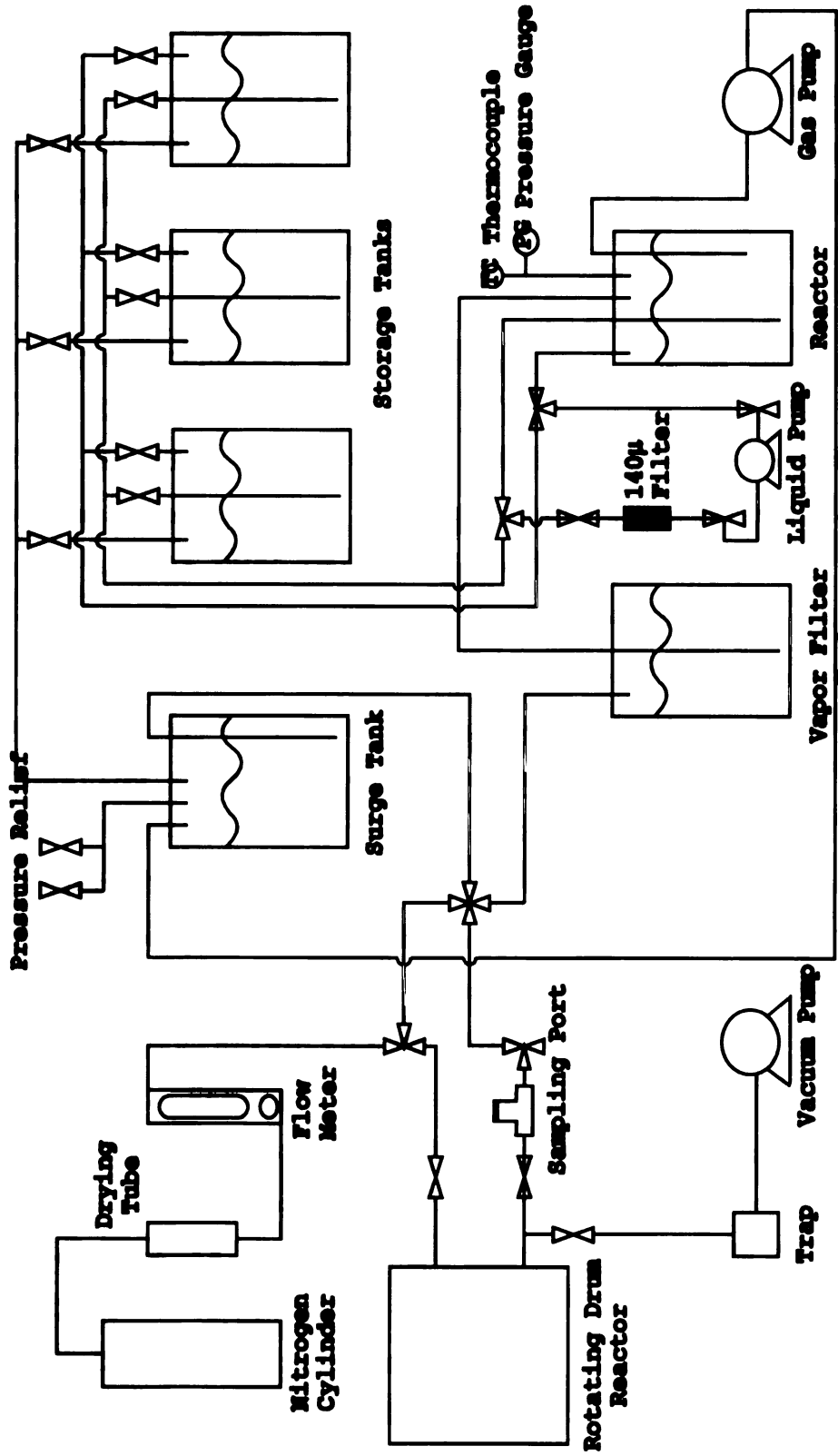

Figure 5: Schematic Diagram of Sulfonation System

The surface composition of sulfonated and nonsulfonated resins was characterized by a PHI 5400 ESCA System (Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, Minnesota), at the CMSC. In addition, the sulfonated resins with the exposure time of 5, 8 and 10 min were submitted to Galbraith Laboratories, Inc. (Knoxville, Tennessee) for Elemental Analysis.

2.2 Sample Preparation

2.2.1 Compounding

A Baker Perkins Model ZSK-30, 30 mm, 26:1 co-rotating twin-screw extruder (Werner & Pfleiderer Corporation, Ramsey, New Jersey) at the CMSC was used for homogenizing the compounds. The extruder is composed of five heating zones. The temperature of each heating zone was manipulated via a controlling system. By heating and water-cooling procedures, the heating temperature was maintained. The wood fiber and resin at a 2:3 weight ratio were dryblended in a separate container. The mixture was fed through the feeding zone of the extruder by a Weight-Loss-Differential Weigh Feeder (Acrison, Inc., Moonachie, New Jersey) with a control system of MD II 2000 Weigh Feeder Controller (Werner & Pfleiderer Corporation, Ramsey, New Jersey). The compositions of the composite materials fabricated are shown in Table 2. The operating parameters of the extruder for compounding the mixture were as follows: heating temperature range, 135 to 165 ^{o}C; screw speed, 100 rpm; feed rate, 6.06 to 9.47 gm/min. The parameters for extruding unfilled polypropylene were 170 ^{o}C, 100 rpm and 22.7 to 26.5 gm/min, for heating temperature, screw speed and feed rate, respectively. The

percentage of wood fiber used in all composites was 40% by weight. The materials extruded through the die were cut into bars and cooled by air. The weight and length of each bar was approximately 37 gm and 13 cm, respectively. Purging the retained material from the extruder was done before and after compounding, with pure resin.

Table 2: Composition of Composites and Materials by Weight-Percent

No.	Material Code	Composition
1	NS	60% Nonsulfonated PP / 40% Wood Fiber-1[a]
2	NSn	60% Nonsulfonated PP / 40% Wood Fiber-2[a]
3	S5	60% 5-min Sulfonated PP / 40% Wood Fiber-1
4	S8	60% 8-min Sulfonated PP / 40% Wood Fiber-1
5	S10	60% 10-min Sulfonated PP / 40% Wood Fiber-1
6	S10n	60% 10-min Sulfonated PP / 40% Wood Fiber-2
7	S20n	60% 20-min Sulfonated PP / 40% Wood Fiber-2
8	PP	100% Polypropylene Resin

[a] 1 and 2 refer to the wood fibers from Canfor Panel and Fibre Division, Co. and Georgia-Pacific Corp., respectively.

2.2.2 Compression Molding

The extruded materials were formed into sheets using a Carver Model M Laboratory Press compression molding machine (Fred S. Carver, Inc., Menomonee, Wisconsin). Two sizes of

frames were used: a 150 by 150 by 2.5 mm frame for the tensile samples; and a 127 by 127 by 3.2 mm frame for the impact and flexural samples. The heating temperature of the two platens was set at 170 ^{o}C. The sample bars were sandwiched between metal plates. Polyethylene terephthalate (PET) sheets were placed between the samples and metal plates, both top and bottom sides, in order to prevent sticking to the metal plates and to provide smooth surfaces to the samples. The compression-molded sample was held between the heating platens for 10 min under pressure, which was gradually increased to 35,000 lbs. The system was then cooled down to 28 ^{o}C by circulation of cold water for approximately 20 min.

2.2.3 Sample Cutting

By using a mechanical saw (Jarmac Co., Springfield, Illinois), the molded sheets were cut into test specimens, in the fiber (lengthwise) direction and perpendicular to the fiber (crosswise) direction of the composite materials. For the tensile test, the 150 x 150 x 2.5 mm. sheets were cut into 150 by 20 by 2.5 mm pieces, which were then shaped into Dumbbell Type I specimens using a Tensilkut Model 10-13 Specimen Cutter (Tensilkut Engineering Division Sieburg Industries, Inc., Danbury, Connecticut). The dimensions of the test specimens were as follows: total length, 150 mm; overall width, 20 mm; width of narrow section, 10 mm; and thickness, 2.5 mm. The molded sheets of 127 x 127 x 3.2 mm size were cut into test specimens for flexural and impact testing. The flexural specimens have the dimensions as follows: length, 127 mm; width, 12.7 mm; and thickness, 3.2

mm. The impact specimens were cut into dimensions of 62 mm in length, 12.7 mm in width and 3.2 mm in thickness. The specimens were notched using a TMI Notching Cutter (TMI Testing Machines, Inc., Amityville, New York). The notch angle was 45° and the depth of samples, at notch, was 10.16 mm.

2.3 Mechanical Testing

All specimens were conditioned at 23 °C and 50% RH for at least 40 hours prior to testing. At least seven samples per material per test method were tested at once.

2.3.1 Tensile Test

Tensile strength, percent elongation and modulus of elasticity were measured by an Instron Universal Tensile Tester Model SFM-20 (United Calibration Corporation, Hunting Beach, California) at ambient conditions (23 °C, 50% RH). The ASTM D638-91, Standard Test Methods for Tensile Properties of Plastics (ASTM, 1993), was followed. A laser extensometer was chosen for measuring tensile strength and percent elongation. The test conditions were set as follows: full scale load cell, 1000 lbs; crosshead speed, 0.02 in/min for composites and 1 in/min for original polymer; and gauge length, 2 in. For tensile modulus measurements, a standard extensometer with 1-inch gauge length was employed. The other test conditions were as follows: full scale load cell, 20 lbs; and crosshead speed, 0.02 in/min (2 %/min of the gage length), respectively.

Promptly after the individual test, a computer system interfaced to the Instron Universal tester calculated the tensile properties following the equations given below:

Tensile Strength (at yield or at break), σ

$$\sigma = \frac{P}{A}$$

where: P = maximum load at yield or at break

A = original cross-sectional area

Percent Elongation (at yield or at break), %EG

$$\%EG = \frac{(L - L_o)}{L_o} \times 100$$

where: L = extension at yield or at break

L_o = original gauge length

Modulus of Elasticity, E

$$E = \frac{\Delta P}{\Delta L}$$

where: ΔP = difference of stress corresponding to a linear portion of the load-deflection curve

ΔL = corresponding difference in strain

2.3.2 Flexural Test

Sample flexural strength and flexural modulus were determined by an Instron Universal Tensile Tester Model SFM-20 (United Calibration Corporation, Hunting Beach, California) at ambient conditions (23 °C, 50% RH), following ASTM D790-92, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical

Insulating Materials (ASTM, 1993). Test method I, a three-point loading system was utilized. The parameters of the test were set as follows: load cell, 20 lbs; test speed, 0.05 in/min; and span-to-depth ratio, 16:1. The test was terminated upon sample rupture or at 5% axial strain, depending which came first.

Immediately after the individual test, a computer system interfaced to the Instron Universal tester calculated the tensile properties following the equations given below:

Flexural strength, S

$$S = \frac{3PL}{2bd^2}$$

where: P = load at moment of break

L = support span

b = width of tested specimens

d = depth of tested specimens

Flexural Modulus, E_B

$$E_B = \frac{L^3 m}{4bd^3}$$

where: m = slope of the tangent of an initial straight-line portion of the load-deflection curve

2.3.3 Impact Test

Notched Izod Impact resistance was determined by a TMI Izod Impact Tester, Model 43-02 (TMI Testing Machines, Inc., Amityville, New York) at ambient conditions (23 ^{o}C, 50% RH).

The 5 ft-lb pendulum weight was used. The testing was conducted in accordance with the ASTM D256-92, Standard Test Methods for Impact Resistance of Plastics and Electrical Insulating Materials (ASTM 1993). The machine automatically calculated and reported the impact strength value, which is the energy required to break the sample. Mathematically, an impact strength is represented by the area under the stress-strain curve until the rupture point.

2.4 Water Sorption Studies

The dumbbell-shape specimens--prepared in the same manner as tensile specimens--of NS, S5, S8, S10 and PP in the fiber direction were utilized in this study. These specimens were stored in a chamber of controlled temperature and relative humidity, at 35 ^{o}C and 90 % RH. The samples were weighed at predetermined intervals of 0, 1, 3, 5, 7 and 9 weeks, respectively. The water (if any) on the surface was wiped off with a paper towel and weight measurements were performed immediately. The percentage of weight increase (or water sorption) was calculated by the following equation:

$$\text{Weight Increase, \%} = \frac{W - W_o}{W_o} \times 100$$

where: W = sample weight after storaged

W_o = original sample weight

After 3, 5, 7 and 9 weeks storage, five to seven samples of each material were withdrawn for tensile testing. The tensile strength was evaluated following the ASTM D638-91 (ASTM, 1993).

2.5 Density Measurement

Density of all composites was determined using a water displacement method. Long strips of approximately 115 x 12 x 2.5 mm dimensions were cut from the molded sheets. The weight of every sample was measured. A graduated cylinder (25 ml), containing clean water without bubbles, was used for measuring the volume of the samples. Each sample was put in the cylinder individually. The increased level of water in the cylinder due to water displacement was equal to the sample volume. The level of water in the cylinder was read before and after the displacement. The weight divided by the volume value of each sample was reported as a density of the respective sample.

2.6 Statistical Analysis

SPSS® for Windows™ Student Version (Release 6.0.1) Software program was used to perform statistical analyses. The procedure chosen was a one-way analysis of variance with the Tukey-HSD test to determine the statistical significance of the numerical data obtained in this study, at a 95% confidence interval. The analysis was performed on: (i) all mechanical properties--such as tensile properties, flexural properties and impact properties--between composite groups in both lengthwise and crosswise directions, as well as between two fiber directions of each composite material; and (ii) the tensile strength data between material groups for each storage time, and between storage conditions for each material type.

RESULTS AND DISCUSSION

1. Surface Characteristic

The surface composition of nonsulfonated and sulfonated PP resin samples, determined by Electron Spectroscopy for Chemical Analysis (ESCA), are presented as the percentage of atomic concentration and the relative atomic ratios in Tables 3 and 4, respectively. The sulfur concentrations determined by ESCA and by Elemental Analysis are reported as a function of reaction time in Table 5.

The atomic concentrations of carbon, C, oxygen, O, nitrogen, N, and sulfur, S, are reported for various sulfonation-time treatments (0 to 20 minutes) of the polypropylene resin. The presence of silicon, Si, was found in the resin of 0-min and 5-min sulfonation time (not reported). This was attributed to contamination during sample preparation and handling. The oxygen found in the nonsulfonated resin is thought to be due to oxidation of the resin during processing. Table 4 presents the relative atomic ratios obtained for the respective sulfonated samples, which illustrate the chemical change occurring on the surface during the sulfonation process. The ratios were in accordance with the theoretical molecular structure of the sulfonate group. For instance, with an increased reaction time, the ratios of O/S and N/S remain relatively constant, at approximately 3 to 1 and 1 to 1, respectively. The results support the presence of

sulfonic acid functional groups on the polymer backbone, and their complete neutralization by NH_3 occurring. The ammonium sulfonate group ($-SO_3^-NH_4^+$) on the polymer backbone, as a theoretical outcome of the sulfonation reaction, is depicted in Figure 6. The C/S ratio was found to decrease as the sulfonation time increased. This finding indicated that higher sulfonation levels on the PP resin were achieved when reaction time was extended. In addition, the C/S ratio approached a constant value, 28 to 1, at 10-min sulfonation time.

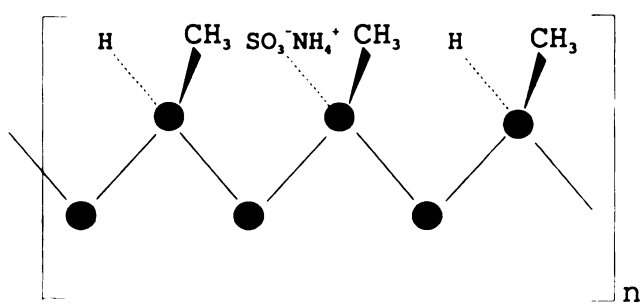

Figure 6: Theoretical Molecular Structure of Sulfonated PP

Asthana (1993) proposed that there was a limitation for the sulfonation of polypropylene and that sulfonation beyond the limiting level could result in degradative reactions on the polymer surface, such as chain scission. At the molecular level, chain movement due to the incorporation of $SO_3^-NH_4^+$

Table 3: Atomic Concentration for Nonsulfonated and Sulfonated PP Resins by ESCA Analysis

Sample	Percentage Atomic Concentration			
	Carbon, C	Oxygen, O	Nitrogen, N	Sulfur, S
0 min	98	1.4	-	-
5 min	95	3	0.9	0.8
8 min	93	4.5	0.9	1.2
10 min	85	8	4	3
10 min[a]	85	8	4	3
20 min[a]	83	10	4	3

[a] : reduced level of resin charge in the rotating drum reactor

Table 4: Relative Atomic Ratios of Sulfonated PP Resins

Sample	C/S	O/S	N/S
0 min	-	-	-
5 min	118.8	3.8	1.1
8 min	77.5	3.8	0.8
10 min	28.3	2.7	1.3
10 min[a]	28.3	2.7	1.3
20 min[a]	27.7	3.3	1.3

[a] : reduced level of resin charge in the rotating drum reactor

Table 5: Comparison of Sulfur Content Determined by ESCA Analysis and Elemental Analysis, as a function of Sulfonation Time

Sample	Atomic % Sulfur (ESCA)	Total % Sulfur Per Gram of Resin (Elemental)
0-min	0	N/A
5-min	0.8	< 0.05
8-min	1.2	< 0.05
10-min	3	< 0.05
10 min[a]	3	N/A
20 min[a]	3	N/A

[a] : reduced level of resin charge in the rotating drum reactor

species was impeded by the structure of PP and, therefore, did not allow for additional insertion of sulfonate groups beyond the sulfonation limit (Asthana, 1993). The maximum achieved sulfonation level reported by both Asthana (1993) and Wangwiwatsilp (1993) was found to be one sulfonate group per three repeating monomer units when polypropylene films were utilized. The reaction site on the polypropylene was proposed to be at the tertiary carbon, due to the highly electrophilic reaction with the SO_3 gas (Asthana, 1993). However, in the present study, as shown in Table 4, the highest achieved sulfonation level gave a C/S ratio of 28, which indicated, on average, one sulfur atom per 28 carbon atoms, or approximately 9 propylene monomer units per

sulfonate group. The results from Asthana (1993) and Wangwiwatsilp (1993) suggested that even though the extent of sulfonation achieved in the present study approached a constant level, the low sulfonation achieved was not limited by the nature of the polypropylene, but to other external factors, which are discussed in more detail in a later section.

As shown graphically in Figure 7, the extent of sulfonation level achieved was found to increase with reaction time. A constant level of sulfur content was reached following a 10-min exposure time. In addition to determining the atomic sulfur content by ESCA, the total sulfur concentration (per gram of resin) determined by elemental analysis for the respective sulfonated resins was also obtained. The total sulfur content achieved was less than 0.05 % by weight, despite the increase in sulfonation level with exposure time. Several attempts at achieving higher levels of sulfonation were carried out, including a reduction of the resin charge to about one third of the original quantity (from 1816 to 681 grams) with reaction times of 10 minutes and 20 minutes, respectively. No further increase in sulfur content was achieved (see Table 5).

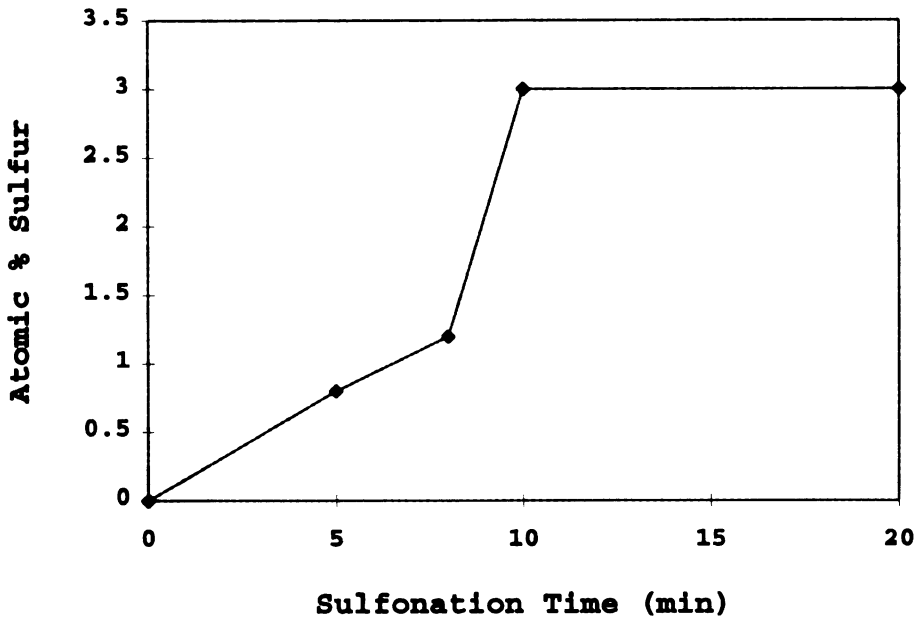

Figure 7: Atomic Percent Sulfur Concentration of PP Resins As a Function of Sulfonation Time

In comparing the sulfonation of the PP resin and PP films, it is necessary to consider other factors such as the sample surface areas and operational differences for each sample. The PP resin, in the form of a powder, had a surface area of 0.09 m^2/g. The total surface area of the PP resin (681 grams) in the rotating drum was 61.29 m^2, whereas the exposed surface area of the PP films (four, 6 x 13 in. films) sulfonated by a batch process (Wangwiwatsilp, 1993) was approximately 0.40 m^2. Thus, the ratio of the surface area of PP resin to PP films per run is approximately 153 to 1. The extremely large surface area of the resin can result in the depletion of the sulfur trioxide concentration, thereby showing no further formation of sulfonate groups with the additional time of sulfonation.

Another reason for the depletion of SO_3 content in the rotating drum reactor is related to the clogging of the sulfur trioxide synthesizer at the location where the sulfur dioxide and air inlets were connected to the system. The SO_3 synthesizer is the unit in which the reaction of SO_2 and air occurred at 427 ^oC, in the presence of a catalyst, to produce SO_3 for the SO_3 generator. The clogging of the inlet lines was attributed to the presence of a desiccant ($CaSO_4$) at the base of the catalyst bed which was included to remove any moisture from the feed lines prior to catalytic oxidation of the SO_2 to yield SO_3 for sulfonation. The clogging resulted in a lower supply rate of SO_3 to the storage tanks, which in turn lowered the capacity of the SO_3 generator in supplying SO_3 for the sulfonation reaction. Sulfonation of the PP resin required a larger quantity of

SO_3 due to the extremely high surface area of the resin sample charged into the reactor, as compared to that of the PP films. This problem was discovered at the completion of the present study and may be the root cause of the low levels of sulfonation achieved. Moreover, films used as a substrate can provide total exposure of the film surface to the SO_3 gas in the sulfonation chamber. In contrast, it is difficult to control the amount of exposed surface for the powdered resin. Through proper agitation in the rotating drum and by controlling the amount of charge weight of the resin in the reactor, together with maintaining a sufficient SO_3 level, the sulfonation reaction on the polypropylene resin may be optimized to achieve the maximum expected level.

2. Density of Composites

The density values were determined for nonsulfonated and sulfonated composites fabricated with wood fibers from two suppliers. At least eight replicate analyses were performed for each sample. The mean and standard deviation for the density data of the respective composites are summarized in Table 6. The detailed data are presented in Appendix C, Table 15. A one-way analysis of variance was performed to determine any significant difference of means, at 95% confidence interval. The detailed analysis is presented in Appendix E, Table 24.

The composites from sulfonation times under 10 minutes were approximately equal in density values, with only the density of 20-min sulfonated composites showing statistically significant differences from that of the composites with 0-, 5- and 8-min sulfonation times. The higher observed density value for 20-min sulfonated composite is assumed to be the result of a variation in the composites' homogeneity from point to point in the compounding process. A difference in wood fiber weight fraction as reflected by the composite homogeneity would be expected to affect the density of the materials directly. Alternatively, although no statistically significant increment showed among sulfonated composites with 10 min. sulfonation time and under, there was a trend of an increased density values of the sulfonated composites, as a reaction time increased. The reaction of the polymer with SO_3 in the sulfonation process resulted in the substitution of sulfonic acid groups for hydrogen atoms. This insertion of SO_3H groups in the polymer backbone can

result in an increase in weight and therefore the density of the composite system. With a longer reaction time, more sulfonate groups were substituted onto the polymer chain, which is the matrix phase in the composites. The sulfonation effect on the density of the respective composites was, however, kept minimal due to the low levels of sulfonation being achieved.

Table 6: Results of Density (g/cc)

Material Code	Material	Mean	Sd.
NS	Nonsulfonated PP/Wood Fiber-1	1.049	0.014
NSn	Nonsulfonated PP/Wood Fiber-2	1.052	0.020
S5	5min Sulfonated PP/Wood Fiber-1	1.053	0.017
S8	8min Sulfonated PP/Wood Fiber-1	1.050	0.011
S10	10min Sulfonated PP/Wood Fiber-1	1.064	0.011
S10n	10min Sulfonated PP/Wood Fiber-2	1.063	0.015
S20n	20min Sulfonated PP/Wood Fiber-2	1.078	0.009

3. Tensile Properties

For the respective composites, tensile strength and percent elongation at fracture moment, and modulus of elasticity were determined in both lengthwise and crosswise fiber directions. The tensile strength and elongation at yield point, as well as modulus of elasticity, were reported for the pure PP polymer parallel to the extrusion flow. The mean and standard deviation of 12 to 14 replications for tensile properties of the respective composites and PP are summarized in Tables 7, 8 and 9, respectively. The results are also depicted graphically in Figures 8, 9 and 10, where the tensile strength, percent elongation and modulus of elasticity data are presented, respectively. The detailed data of the tensile properties are also presented in Appendix C from Table 16 to Table 18. A one-way analysis of variance of tensile properties of the respective composites was performed to determine any significant differences between means, at a 95% confidence interval. The results of the statistical analysis are shown in Appendix E from Table 25 to Table 33.

3.1. Effect of Fiber Direction

The referred to 'lengthwise' and 'crosswise' fiber directions were based on the assumption that the extrusion compounding process can provide the preferred alignment of short fibers in the flow direction of the extrudate, which is regarded as the lengthwise direction. For comparison, the direction perpendicular to the flow is regarded as the crosswise direction. From all tensile data observed, the tensile strength of NSn, S10 and S10n; the percent

elongation of NS, NSn and S5; and modulus of elasticity of NSn composites showed higher values in the lengthwise direction than in the crosswise direction, while there was no statistically significant difference in the tensile properties between the remaining composites as a function of orientation direction. The fibers parallel to the loading axis generally provide composites with higher tensile properties than do fibers in the crosswise direction, due to the load transfer from the matrix through fiber ends and hence a more efficient contribution of fibers to the composite properties. However, the results indicated that only a low degree of uniform fiber orientation was present in the composites from this experiment. The small extent of preferred alignment was probably accounted for by the pronounced effect of the shear field, during the extrusion process, producing no net change in fiber orientation, rather than the fiber rotation by the elongational field. Also, fibers were shortened because of fiber breakage during the extrusion process. In practice, it is difficult to satisfactorily control the fiber direction during the extrusion process. Fibers tended to be aligned in a random fashion, which produced composites more or less as an isotropic material. Even though statistical differences were found between fiber directions in some cases, composites with a large degree of aligned fibers usually give markedly higher mechanical properties i.e. tensile strength and modulus, for samples aligned parallel to the fiber direction. A possible reason for the somewhat lower properties observed in the crosswise samples is that the sheet formed from the extruded bars did not have good

bonding when molded by the compression molding procedure. Similar findings were also presented by Haraguchi (1993) for polyethylene/ wood fiber composites. Another reason for the lower properties observed might be the low homogeneity achieved in the mixing process, resulting in a wide deviation in properties.

3.2. Effect of Sulfonation

The tensile properties of both nonsulfonated and sulfonated composites were compared, as a function of sulfonation time, within the composite system for each type of wood fibers used. Thus, the evaluation was focused on two sets of composites: (i) NS, S5, S8 and S10; and (ii) NSn, S10n and S20n. Based on statistical analysis, the observations with respect to tensile strength, percent elongation and modulus of elasticity properties of the composites are summarized as follows:

(1) The tensile strength values were: (i) improved for samples S5 and S8 over sample NS in both the lengthwise and crosswise directions; (ii) increased for sample S10 over sample NS in the lengthwise direction; (iii) increased for sample S10n over sample NSn in the crosswise direction; (iv) increased for sample S20n over sample NSn in both directions; (v) equivalent between samples S5 and S8 in the lengthwise direction and between samples S5, S8 and S10 in the crosswise direction; and (vi) equivalent between samples S10n and S20n for both fiber directions.

(2) The percent elongation values were: (i) lower for sample S5 than for sample NS in both the lengthwise and

crosswise directions; (ii) lower for samples S8 and S10 than for sample NS in the lengthwise direction; (iii) lower for sample S10n than for sample NSn in the lengthwise direction; (iv) lower for sample S20n than for sample NSn in both directions; (v) equivalent among samples S5, S8 and S10 in the lengthwise direction and between samples S8 and S10 in the crosswise direction; and (vi) equivalent between samples S10n and S20n in both fiber directions.

(3) The modulus of elasticity values were: (i) equivalent among samples NS, S5 and S10 in both the lengthwise and crosswise directions; (ii) higher for sample S8 than for sample S10 in the lengthwise direction; and (iii) equivalent among samples NSn, S10n and S20n in both directions.

There was a variation of the resultant mechanical properties of the respective composite structures. Nevertheless, the findings showed that sulfonation had a statistically significant effect on the enhancement of tensile strength, and little or no effect on the improvement of the other tensile properties evaluated for the composites. The lack of significant improvement of the composite mechanical properties by sulfonation of the PP resin was attributed in part to the low sulfonation level achieved. The levels of sulfonation achieved are thought to contribute minimally to improvement of interfacial interaction between fiber and matrix phases, thereby showing a small influence in enhancing the tensile properties of the resultant composites. Hence, with economical and practical considerations in mind, this achievement did not exhibit any apparent benefit at this time in commercial or industrial

applications. It should be noted, however, that the sulfonation treatment for the enhancement of composite tensile properties still shows potential. For example, examination of the tensile strength data showed a marginal increase for the sulfonated composites, as compared with the nonsulfonated structures. Since PP has shown its capability to achieve higher sulfonation levels via the sulfonation treatment, as reported by previous investigators (Asthana, 1993 and Wangwiwatsilp, 1993), it is assumed that if the optimization of the sulfonation treatment for PP resin was achieved, the higher level sulfonated PP resin could provide a substantial increase in the mechanical properties of the composites, as a result of the improvement of fiber-matrix interfacial interaction.

3.3. Effect of Fiber Type

Fiber-1 and fiber-2 (as described in Materials section) were used as reinforcing fillers for both nonsulfonated and sulfonated composites. To compare the effect of the two fibers on the tensile properties, the following pairs of composite materials were evaluated: (i) samples NS and NSn; and (ii) samples S10 and S10n. Based on statistical analysis, the following conclusions were drawn: (i) In the case of the tensile strength property, there was no statistically significant difference between the NS vs. NSn sample pair and the S10 vs. S10n sample pair, except that the tensile strength of sample NS was higher than that of sample NSn in the crosswise direction; (ii) For percent elongation, a higher percent elongation for sample NSn in both directions was observed, while sample S10n showed a

higher value in the crosswise direction over its respective counterparts. For the lengthwise direction, sample S10n showed no significant difference from sample S10; and (iii) For the modulus of elasticity, no statistically significant difference was found between the NS vs. NSn sample pair, and the S10 vs. S10n sample pair, except for the NS vs. NSn samples in the crosswise direction. The properties of wood fibers can vary greatly among species. In addition, within the same species, the fiber characteristics can differ from batch to batch, when different parts of wood are used. The ways in which fibers are processed, and handled, for example, are important to properties of the fibers (Richardson, 1987). Fiber characteristics such as fiber length, fiber length distribution and fiber aspect ratio can greatly affect the properties of short-fiber composites. The load transmission from matrix to fibers is dependent on the fiber aspect ratio. When the fiber aspect ratio is decreased, the ability of stress transfer also decreases (Hull, 1981). From the findings of the present studies, there was little or no significant difference in tensile properties between fiber-1 and fiber-2 composites. Therefore, the effect of the two fiber types on the tensile properties could be neglected.

Table 7: Results of Tensile Strength at Break (MPa)

Material Code	Material	Fiber Direction	Mean	Sd.
NS	Nonsulfonated PP/Wood Fiber-1	Lengthwise	16.29	1.33
NS	Nonsulfonated PP/Wood Fiber-1	Crosswise	15.56	1.43
NSn	Nonsulfonated PP/Wood Fiber-2	Lengthwise	16.46	0.94
NSn	Nonsulfonated PP/Wood Fiber-2	Crosswise	13.35	1.55
S5	5min Sulfonated PP/Wood Fiber-1	Lengthwise	19.17	1.51
S5	5min Sulfonated PP/Wood Fiber-1	Crosswise	18.61	2.22
S8	8min Sulfonated PP/Wood Fiber-1	Lengthwise	19.04	1.50
S8	8min Sulfonated PP/Wood Fiber-1	Crosswise	18.01	1.19
S10	10min Sulfonated PP/Wood Fiber-1	Lengthwise	18.74	1.81
S10	10min Sulfonated PP/Wood Fiber-1	Crosswise	17.13	1.70
S10n	10min Sulfonated PP/Wood Fiber-2	Lengthwise	17.84	1.42
S10n	10min Sulfonated PP/Wood Fiber-2	Crosswise	16.01	2.36
S20n	20min Sulfonated PP/Wood Fiber-2	Lengthwise	19.31	1.13
S20n	20min Sulfonated PP/Wood Fiber-2	Crosswise	19.15	1.69
PP	Virgin PP		33.32[a]	0.26

[a] Reported as tensile strength at yield

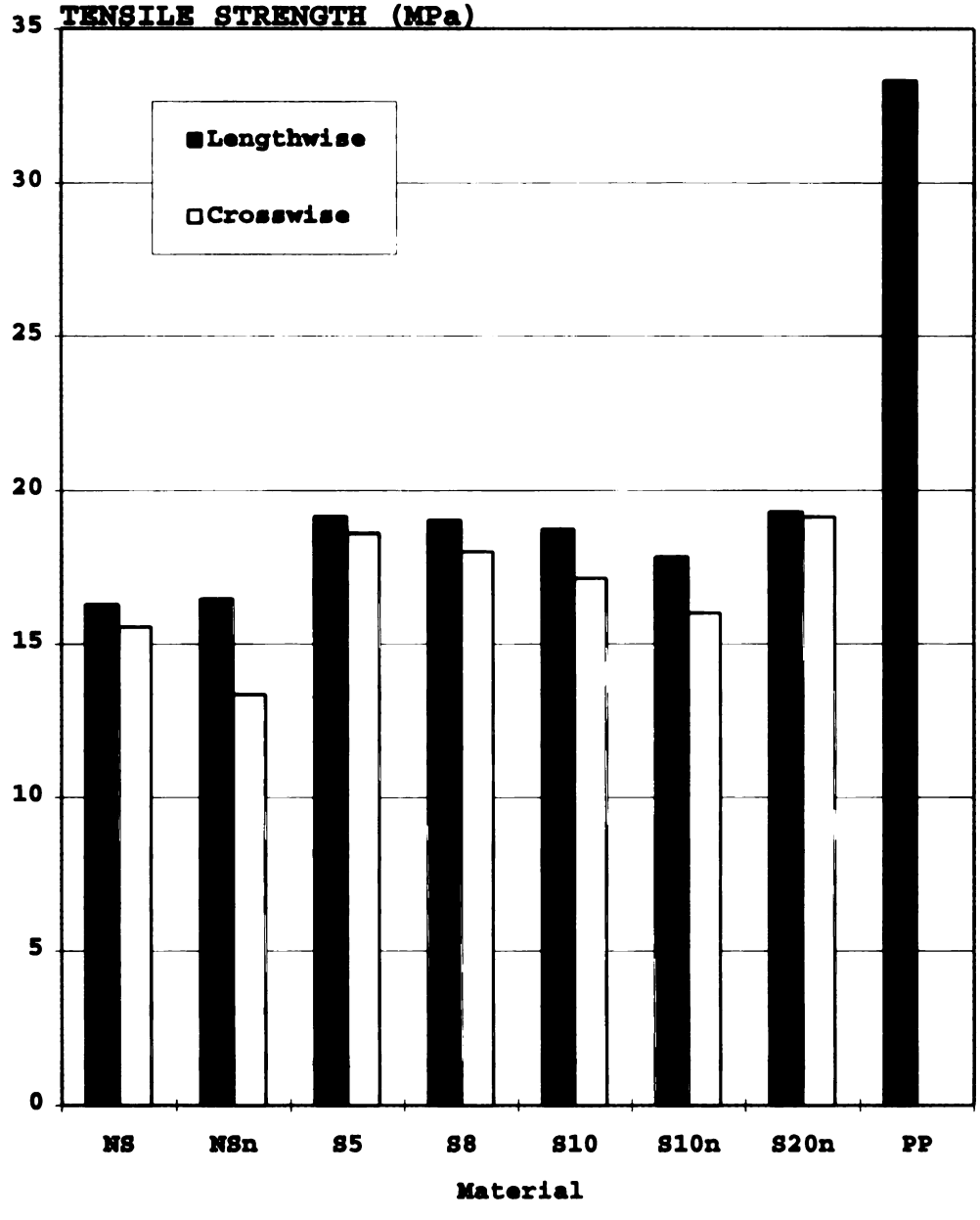

Figure 8: Tensile Strength at Break (MPa)

Table 8: Results of Percent Elongation at Break

Material Code	Material	Fiber Direction	Mean	Sd.
NS	Nonsulfonated PP/Wood Fiber-1	Lengthwise	2.90	1.10
NS	Nonsulfonated PP/Wood Fiber-1	Crosswise	1.69	0.74
NSn	Nonsulfonated PP/Wood Fiber-2	Lengthwise	4.67	1.04
NSn	Nonsulfonated PP/Wood Fiber-2	Crosswise	2.39	0.63
S5	5min Sulfonated PP/Wood Fiber-1	Lengthwise	1.43	0.45
S5	5min Sulfonated PP/Wood Fiber-1	Crosswise	1.09	0.29
S8	8min Sulfonated PP/Wood Fiber-1	Lengthwise	1.35	0.28
S8	8min Sulfonated PP/Wood Fiber-1	Crosswise	1.31	0.31
S10	10min Sulfonated PP/Wood Fiber-1	Lengthwise	1.72	0.46
S10	10min Sulfonated PP/Wood Fiber-1	Crosswise	1.30	0.61
S10n	10min Sulfonated PP/Wood Fiber-2	Lengthwise	2.26	0.61
S10n	10min Sulfonated PP/Wood Fiber-2	Crosswise	1.94	0.52
S20n	20min Sulfonated PP/Wood Fiber-2	Lengthwise	1.75	0.30
S20n	20min Sulfonated PP/Wood Fiber-2	Crosswise	1.71	0.35
PP	Virgin PP		8.85[a]	0.36

[a] Reported as percent elongation at yield

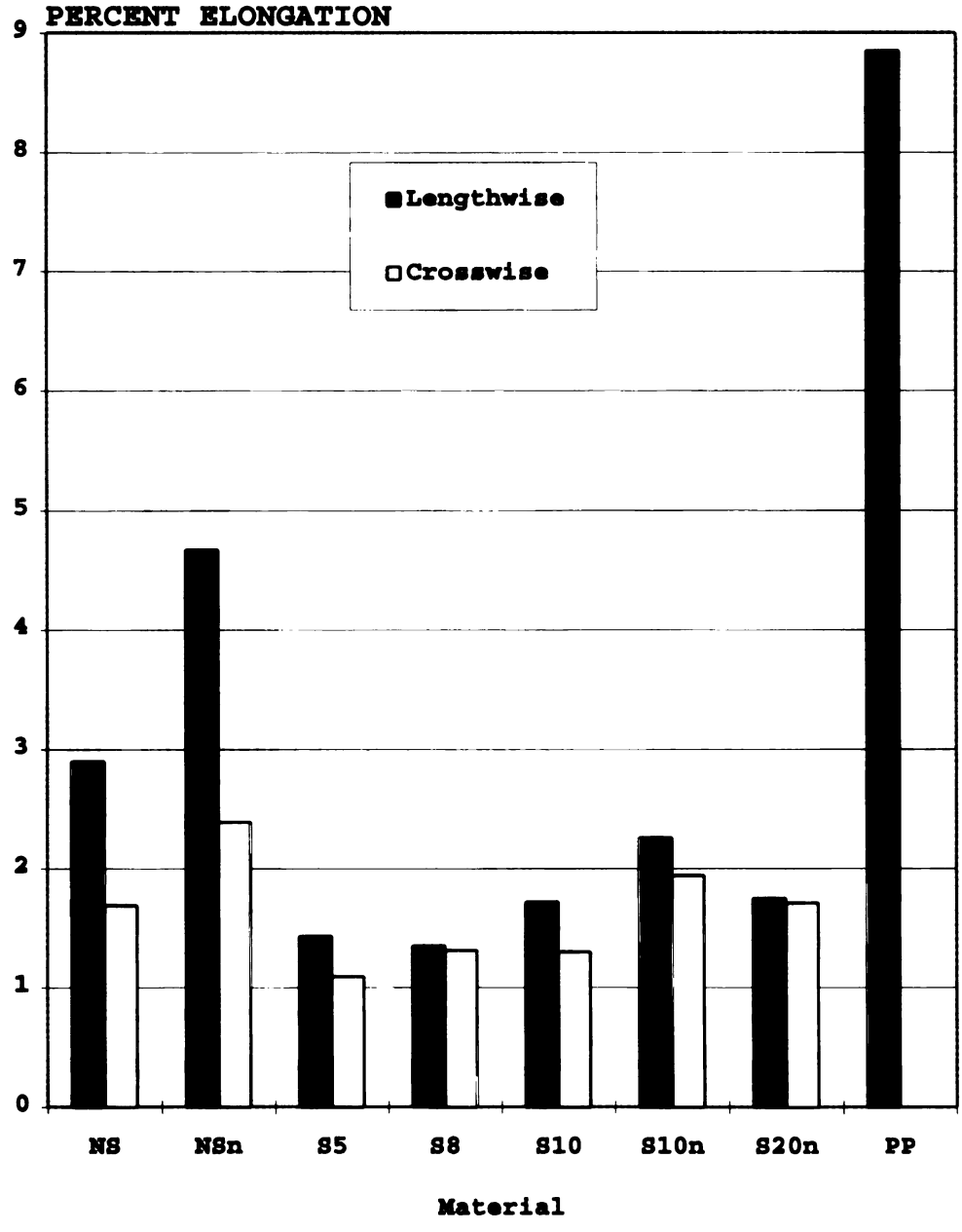

Figure 9: Percent Elongation at Break

Table 9: Results of Modulus of Elasticity (MPa)

Material Code	Material	Fiber Direction	Mean	Sd.
NS	Nonsulfonated PP/Wood Fiber-1	Lengthwise	3281	340
NS	Nonsulfonated PP/Wood Fiber-1	Crosswise	3088	276
NSn	Nonsulfonated PP/Wood Fiber-2	Lengthwise	2856	383
NSn	Nonsulfonated PP/Wood Fiber-2	Crosswise	2493	469
S5	5min Sulfonated PP/Wood Fiber-1	Lengthwise	3408	594
S5	5min Sulfonated PP/Wood Fiber-1	Crosswise	3122	537
S8	8min Sulfonated PP/Wood Fiber-1	Lengthwise	3472	413
S8	8min Sulfonated PP/Wood Fiber-1	Crosswise	3487	496
S10	10min Sulfonated PP/Wood Fiber-1	Lengthwise	3005	376
S10	10min Sulfonated PP/Wood Fiber-1	Crosswise	3034	517
S10n	10min Sulfonated PP/Wood Fiber-2	Lengthwise	2780	149
S10n	10min Sulfonated PP/Wood Fiber-2	Crosswise	2845	315
S20n	20min Sulfonated PP/Wood Fiber-2	Lengthwise	2927	435
S20n	20min Sulfonated PP/Wood Fiber-2	Crosswise	2824	383
PP	Virgin PP		1725	176

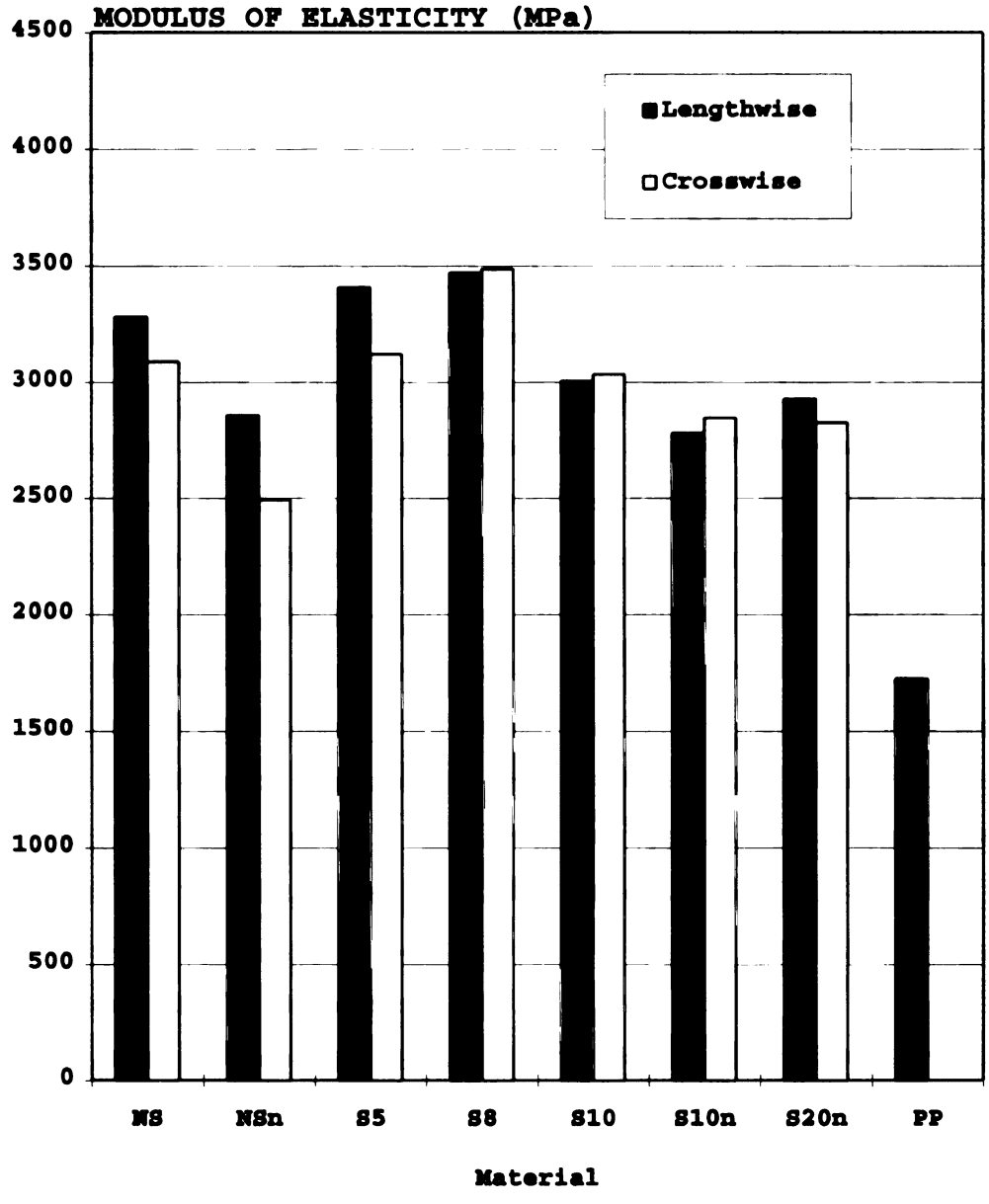

Figure 10: Modulus of Elasticity (MPa)

4. Flexural Properties

Flexural strength and flexural modulus were determined in both lengthwise and crosswise fiber directions for the respective composites. The flexural modulus value for pure polypropylene was determined in the direction parallel to the extrusion flow. The mean and standard deviation of 12 to 16 replications for flexural properties of the respective composites and PP were determined and are tabulated in Tables 10 and 11. The results are also illustrated graphically in the histograms shown in Figures 11 and 12, where the flexural strength and flexural modulus data are plotted, respectively. The detailed data of the flexural properties are also presented in Appendix C in Tables 19 and 20. A one-way analysis of variance of flexural properties of the respective composites was performed to determine any significance between means, at a 95% confidence interval. The results of the statistical analysis are summarized in Appendix E in Tables 34 to 39, respectively.

4.1 Effect of Fiber Direction

None of the composites exhibited a statistically significant difference in flexural strength between lengthwise and crosswise directions, except for samples NSn and S10, which showed higher flexural strength in the lengthwise direction. For flexural modulus, samples NS, NSn, S10 and S10n, in the lengthwise direction, exhibited higher values than those in the crosswise direction, whereas the other composites gave equivalent flexural modulus values in both directions. These findings suggested that the orientation of fibers did not seem to be predominant in the direction of extrusion flow,

but were more likely in a random fashion. The differences observed between the values in the crosswise and lengthwise directions may be due in part to the lack of bonding between the extruded bars during the compression molding step to form the test sheets, as well as to the nonhomogeneity of the compounding step.

4.2 Effect of Sulfonation

The flexural properties of both nonsulfonated and sulfonated composites were compared as a function of sulfonation time, within the composite system for the two wood fiber types used. Thus, the evaluation was focused on two sets of composites: (i) samples NS, S5, S8 and S10; and (ii) samples NSn, S10n and S20n. Based on statistical analysis, the observations, with respect to flexural strength and flexural modulus of the composites, are summarized as follows: (i) For flexural strength, sample S10 displayed a higher value than sample NS in the lengthwise fiber direction; (ii) In the crosswise direction, samples S10n and S20n showed higher flexural strength than sample NSn; (iii) No significant difference between samples S5, S8 and S10 was observed in either direction; (iv) For flexural modulus in the crosswise direction, samples S10n and S20n exhibited higher values than sample NSn; and (v) Sample S5 gave a higher modulus value than samples S10 and NS in the crosswise direction. The other samples showed no statistically significant difference in flexural property values within the group. The poor interfacial adhesion between fiber and matrix was not likely to be overcome by the low extent of sulfonation achieved for the sulfonated PP samples. Thus, the properties

of the sulfonated composites were comparable to the nonsulfonated materials. However, it should be noted that a marginal increase in flexural strength was observed for samples S10, S10n and S20n, respectively. These findings provide supportive evidence of the potential effect of sulfonation on the mechanical properties of polymer/wood fiber composites, if a higher degree of sulfonation of PP is achieved.

4.3 Effect of Fiber Type

To provide a comparison of the effect of fiber-1 and fiber-2 on the flexural properties, the following pairs of composite materials were evaluated: (i) samples NS and NSn; and (ii) samples S10 and S10n. Based on statistical analysis, the conclusions drawn are as follows: For flexural strength, no significant difference was found between samples NS vs. NSn and samples S10 vs. S10n in both the lengthwise and crosswise directions. For flexural modulus, only sample NS afforded higher values than NSn in both directions. The results showed little or no influence of fiber type on the composites' flexural properties.

Table 10: Results of Flexural Strength (MPa)

Material Code	Material	Fiber Direction	Mean	Sd.
NS	Nonsulfonated PP/Wood Fiber-1	Lengthwise	38.54	3.26
NS	Nonsulfonated PP/Wood Fiber-1	Crosswise	37.36	4.16
NSn	Nonsulfonated PP/Wood Fiber-2	Lengthwise	40.40	2.72
NSn	Nonsulfonated PP/Wood Fiber-2	Crosswise	34.65	4.31
S5	5min Sulfonated PP/Wood Fiber-1	Lengthwise	41.74	2.54
S5	5min Sulfonated PP/Wood Fiber-1	Crosswise	39.67	3.39
S8	8min Sulfonated PP/Wood Fiber-1	Lengthwise	40.06	3.76
S8	8min Sulfonated PP/Wood Fiber-1	Crosswise	40.27	2.64
S10	10min Sulfonated PP/Wood Fiber-1	Lengthwise	42.58	3.58
S10	10min Sulfonated PP/Wood Fiber-1	Crosswise	39.36	3.46
S10n	10min Sulfonated PP/Wood Fiber-2	Lengthwise	42.49	3.37
S10n	10min Sulfonated PP/Wood Fiber-2	Crosswise	41.03	3.74
S20n	20min Sulfonated PP/Wood Fiber-2	Lengthwise	41.51	2.58
S20n	20min Sulfonated PP/Wood Fiber-2	Crosswise	43.28	4.03

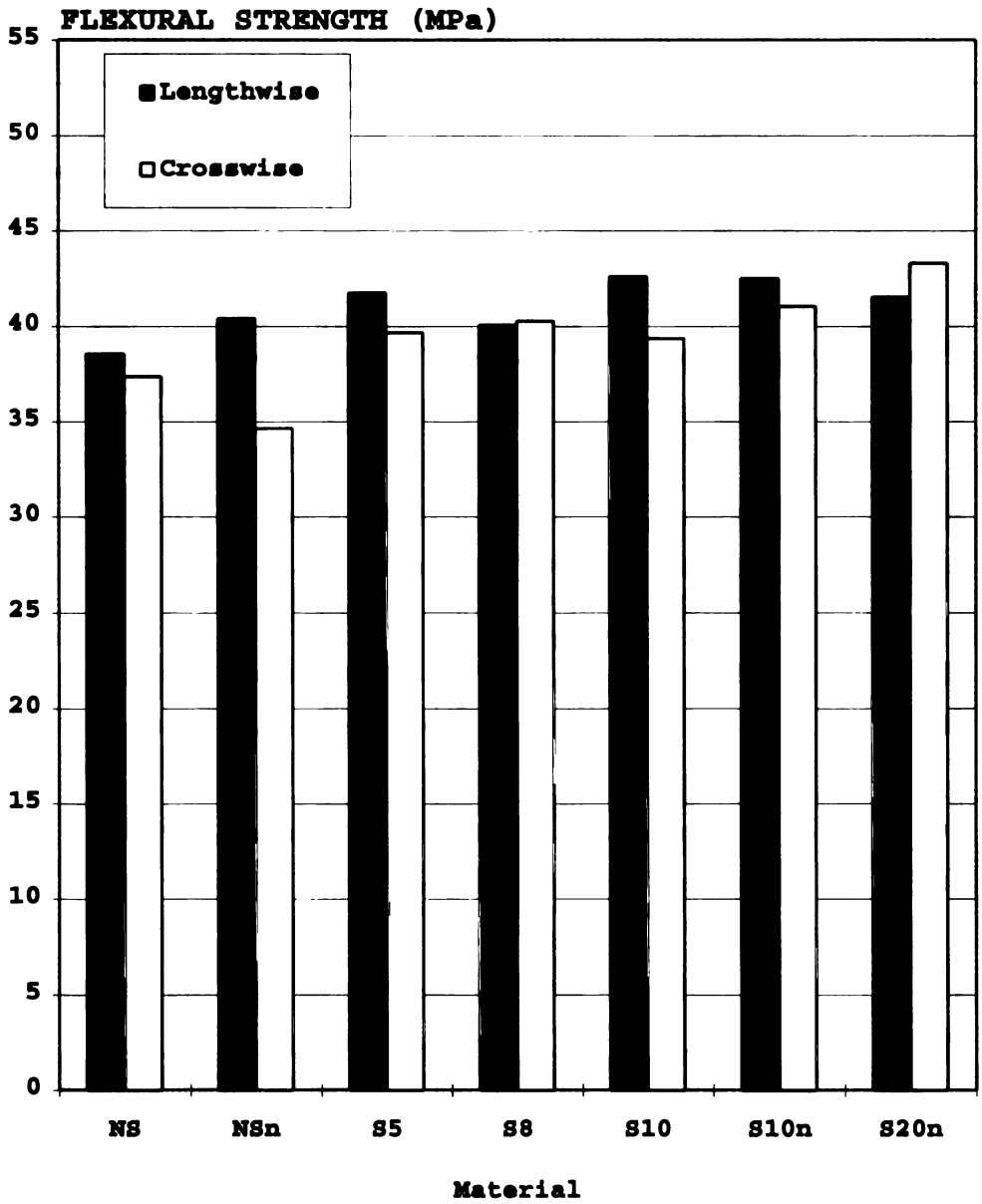

Figure 11: Flexural Strength (MPa)

Table 11: Results of Flexural Modulus (MPa)

Material Code	Material	Fiber Direction	Mean	Sd.
NS	Nonsulfonated PP/Wood Fiber-1	Lengthwise	3017	205
NS	Nonsulfonated PP/Wood Fiber-1	Crosswise	2719	246
NSn	Nonsulfonated PP/Wood Fiber-2	Lengthwise	2610	318
NSn	Nonsulfonated PP/Wood Fiber-2	Crosswise	2374	143
S5	5min Sulfonated PP/Wood Fiber-1	Lengthwise	2995	112
S5	5min Sulfonated PP/Wood Fiber-1	Crosswise	3096	165
S8	8min Sulfonated PP/Wood Fiber-1	Lengthwise	2927	202
S8	8min Sulfonated PP/Wood Fiber-1	Crosswise	2900	222
S10	10min Sulfonated PP/Wood Fiber-1	Lengthwise	2990	164
S10	10min Sulfonated PP/Wood Fiber-1	Crosswise	2823	161
S10n	10min Sulfonated PP/Wood Fiber-2	Lengthwise	2824	170
S10n	10min Sulfonated PP/Wood Fiber-2	Crosswise	2707	141
S20n	20min Sulfonated PP/Wood Fiber-2	Lengthwise	2720	192
S20n	20min Sulfonated PP/Wood Fiber-2	Crosswise	2800	194
PP	Virgin PP		1454	140

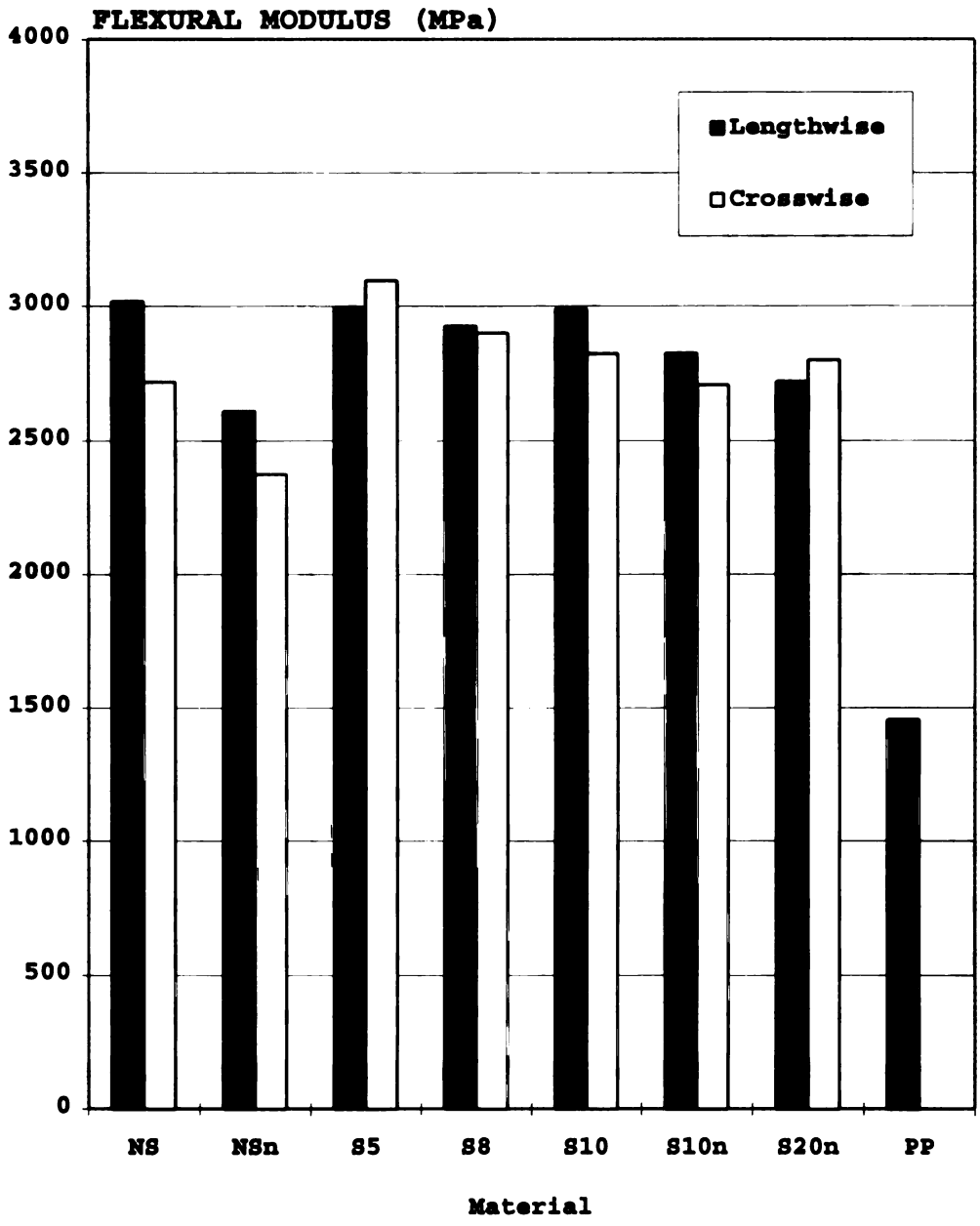

Figure 12: Flexural Modulus (MPa)

5. Izod Impact Strength

Izod impact strength was determined in both the lengthwise and crosswise fiber directions for the respective composites, and also determined for pure PP. The mean and standard deviation of 16 replications for impact strength data of the respective composites and pure PP are summarized in Table 12, and are presented graphically in Figure 13. The detailed results of the impact strength test are summarized in Appendix C, Table 21. A one-way analysis of variance of impact strength of the respective composites was performed to determine any statistically significant difference between means, at a 95% confidence interval. The results of statistical analysis are shown in Appendix E, Tables 40 and 42.

5.1 Effect of Fiber Direction

The impact strength values of sample NS in the crosswise direction and samples S8, S10 and S20n in the lengthwise direction were statistically higher than the impact strength values for the sample measured in the other fiber direction. The impact strength values of S5 and S10n did not display any significant difference between lengthwise and crosswise directions. A slight difference in the impact properties between the two fiber directions may be due to the fact that, as discussed earlier, a preferred alignment in the direction of the extrudate flow may occur to a small degree, such that the fibers were oriented equally in both the direction parallel and perpendicular to the extrudate flow.

5.2 Effect of Sulfonation

The impact strength of nonsulfonated and sulfonated composites was compared within the composite system fabricated from wood fiber-1. For composites fabricated with wood fiber-2, only impact values for sulfonated composites were considered, since no values for the nonsulfonated composite were determined. Thus, the evaluations were on the following groups: (i) samples NS, S5, S8 and S10; and (ii) samples S10n and S20n. The results of statistical analysis, are as follows: (i) sample S10 gave a higher impact strength value in the lengthwise direction than samples NS, S5 and S8; (ii) no statistical difference was found between samples NS, S5 and S8 in the lengthwise direction; (iii) samples NS and S10 gave higher impact values than samples S5 and S8 in the crosswise direction; (iv) sample S10n gave higher impact values than sample S20n in both directions. The findings showed that the effect of sulfonation on impact strength was minimal for the sulfonated composite structures. This was thought to be due in part to the low sulfonation levels achieved. Still, it was found that samples S10 and S10n showed a positive effect of sulfonation. The polar characteristics of the sulfonated PP resulted in an enhancement in interfacial interaction between the polymer and the wood fibers. This yielded an increase in the mechanical properties of the composite structures. Moreover, the impact strength values were also influenced by the geometry of the tested specimens and the notch size and radii. These factors could result in variation from one sample to another, and could account for the difference between samples S10n and S20n. During the impact,

deformation of the ductile matrix and its ability to absorb energy is interrupted by the discontinuity of the fiber phase. Thus, the fibrous composites would exhibit lower impact resistance than the unfilled polymer. However, the impact strength of PP polymer was not as high as expected (see Table 1). This could result from a change in the crystalline fraction of the polymer, during heat processing (extrusion). It is well known that the hydrogen at the tertiary carbon of PP is susceptible to degradative oxidation reactions, such as chain scission, especially when exposed to heat.

5.3 Effect of Fiber Type

To compare the effect of fiber-1 and fiber-2, the pair of composite materials evaluated were S10 vs. S10n. Based on statistical analysis, the results showed no statistically significant difference between the impact strength values for samples S10 and S10n in either the lengthwise or crosswise directions. The results indicated that the impact strength was independent of the fiber type.

Table 12: Results of Izod Impact Strength (J/m)

Material Code	Material	Fiber Direction	Mean	Sd.
NS	Nonsulfonated PP/Wood Fiber-1	Lengthwise	20.65	2.03
NS	Nonsulfonated PP/Wood Fiber-1	Crosswise	22.54	0.86
NSn	Nonsulfonated PP/Wood Fiber-2	Lengthwise	-[a]	-[a]
NSn	Nonsulfonated PP/Wood Fiber-2	Crosswise	-[a]	-[a]
S5	5min Sulfonated PP/Wood Fiber-1	Lengthwise	20.68	1.31
S5	5min Sulfonated PP/Wood Fiber-1	Crosswise	20.45	1.61
S8	8min Sulfonated PP/Wood Fiber-1	Lengthwise	21.60	2.18
S8	8min Sulfonated PP/Wood Fiber-1	Crosswise	19.81	0.93
S10	10min Sulfonated PP/Wood Fiber-1	Lengthwise	26.67	3.58
S10	10min Sulfonated PP/Wood Fiber-1	Crosswise	24.14	2.73
S10n	10min Sulfonated PP/Wood Fiber-2	Lengthwise	24.53	2.52
S10n	10min Sulfonated PP/Wood Fiber-2	Crosswise	25.40	1.31
S20n	20min Sulfonated PP/Wood Fiber-2	Lengthwise	21.35	1.81
S20n	20min Sulfonated PP/Wood Fiber-2	Crosswise	19.28	1.59
PP	Virgin PP		20.49	3.15

[a] No reported data, due to the errors in the experiment.

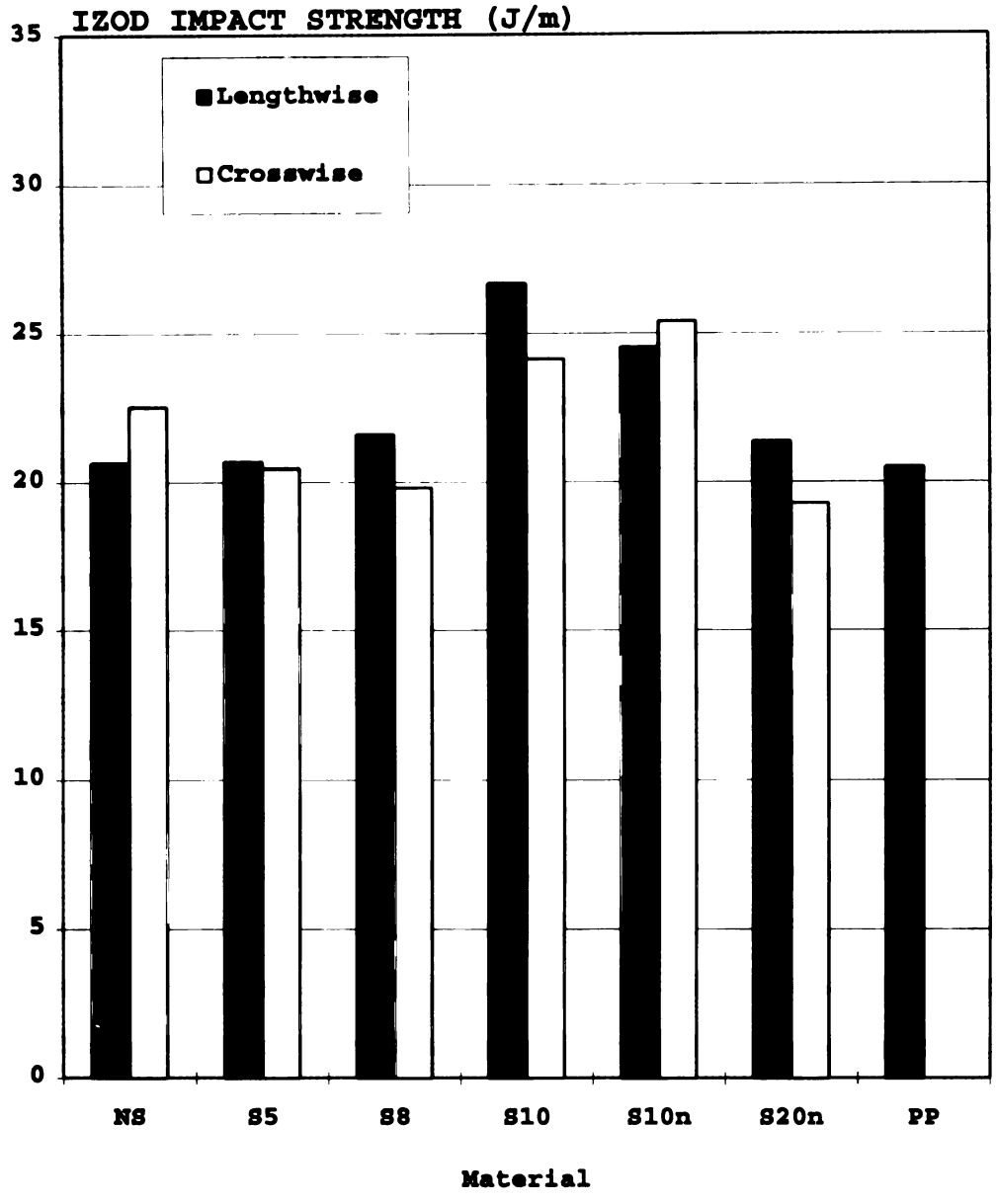

Figure 13: Izod Impact Strength (J/m)

6. Water Sorption Studies

Water vapor sorption by the nonsulfonated and sulfonated composites of fiber-1 was determined and reported as percentage of weight increase versus storage time, as shown in Figure 14. The tensile strength values of the respective composites were determined as a function of storage time and are summarized in Table 13. The results are also illustrated graphically in Figure 15. The detailed data are presented in Appendix D, in Tables 22 and 23, respectively. A one-way analysis of variance was performed to determine any significant difference between the population means of tensile data for each treatment, at a 95% confidence interval. The results of the analysis are summarized in Appendix E, in Tables 43 and 44, respectively.

6.1 Weight Increase

All of the composite structures tested showed a weight increase due to the water uptake as a function of storage time, when exposed to the humidified conditions (35 ^{o}C, 90% RH). Within 7 to 9 weeks, the weight increase reached a steady state or equilibrium level of water sorption. Overall, the maximum amount of water uptake was approximately 2.2 to 2.5% by weight, which is due primarily to water sorption by the wood fibers in the composites. As previously mentioned (see in Materials section), the wood fibers are hydrophilic and hygroscopic in nature, which readily form hydrogen bonds with water molecules and the hydroxyl groups on the fiber chains. Thus, wood fiber composites are susceptible to moisture uptake, and potentially fiber swelling due to water sorption leading to

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dimensional changes of the material, as well as a deteriorative effect on their mechanical properties. Similar patterns of water sorption between nonsulfonated (NS) and sulfonated (S5, S8 and S10) composites were observed, which indicated that there was little effect of sulfonation on water sorption by the respective composites. This may be the result of the achievement of low sulfonation levels on the sulfonated PP resin. Further, the molar concentration of sulfonic acid groups inserted onto the polypropylene, as compared to the abundance of available hydroxyl groups from wood fibers, would tend to have little effect on the moisture sorption characteristic of the sulfonated composites. The variation between the sorption curve of the sulfonated composites (i.e. S5 and S8) and that of the nonsulfonated sample may be attributed to low homogeneity in mixing of the composites, which can result in a variation in composition between one sheet and another. For the pure polypropylene sample, no water sorption occurred because PP, with a hydrophobic attribute, is well resistant to the sorption of water vapor.

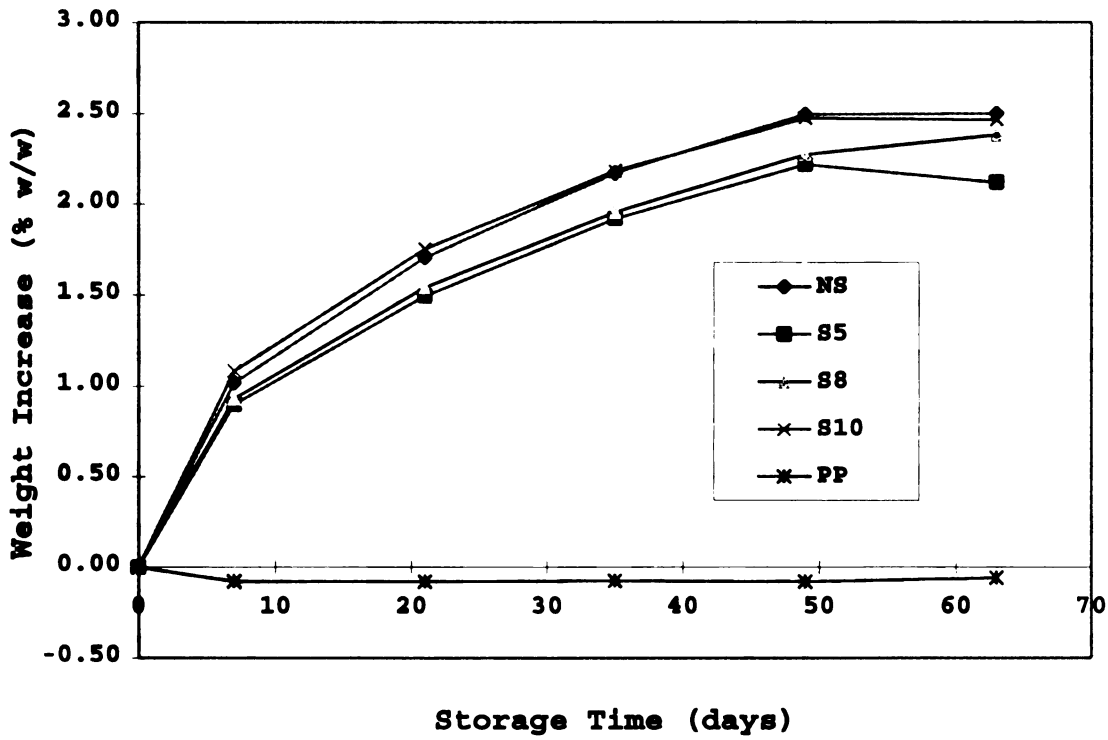

Figure 14: Weight Increase (% w/w) As a Function of Storage Time (days), at 35 °C and 90% RH

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6.2 Tensile Strength

The tensile strength values were measured for the respective composites after 0, 3, 5, 7 and 9-week storage in the 35 ^{o}C, 90% RH conditioned chamber. Only samples with lengthwise fiber direction were evaluated. Based on statistical analysis, the results obtained were as follows: (i) for each of the composites, tensile strength values remained unaffected when stored up to 9 weeks; and (ii) there was no significant difference in tensile strength between samples stored for the same period of time, with the exception of a small increase in tensile strength values for samples S5 and S10 after 7-weeks storage, and sample S5 after 9-weeks storage. Sulfonation of the matrix polymer generally increases the polar contribution to the polymer surface free energy. Therefore, the sulfonated matrix would enhance its compatibility and interaction with wood fiber and, as a consequence, with moisture. However, the effect of humidified conditions on the sulfonated composites was minimal from this study, which could be the result of the low level of sulfonation achieved on the PP matrix polymer.

Tab

Table 13: Tensile Strength Data (MPa) of Samples Stored under Humidified Conditions, at 35°C and 90% RH, for 0, 3, 5, 7, and 9 weeks

Material	Tensile Strength (MPa) at Various Storage Time				
	0-week	3-week	5-week	7-week	9-week
NS	16.29	16.76	16.50	16.15	16.37
S5	19.17	18.54	18.55	19.04	18.97
S8	19.04	17.99	18.50	17.98	17.61
S10	18.74	18.86	18.11	18.22	17.59
PP	33.32	35.44	33.56	35.43	34.41

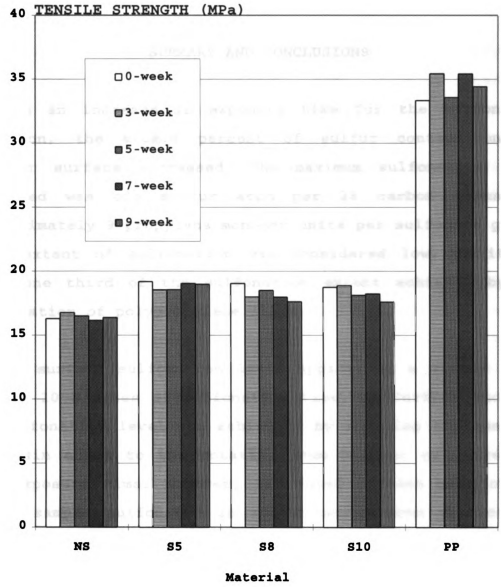


Figure 15: Tensile Strength of Samples Stored under Humidified Conditions, at 35 °C and 90% RH, for o, 3, 5, 7 and 9 weeks

SUMMARY AND CONCLUSIONS

1. With an increase in exposure time for the sulfonation reaction, the atomic percent of sulfur content on the polymer surface increased. The maximum sulfonation level achieved was one sulfur atom per 28 carbon atoms, or approximately 9 propylene monomer units per sulfonate group. This extent of sulfonation was considered low, as it was only one third of the sulfonation extent achieved by the sulfonation of polypropylene films.

2. The surface sulfonation level approached a steady state within 10 minutes of sulfonation time. No further increase in sulfonation level was achieved, by reducing the quantity of resin added to the rotating drum reactor or increasing the exposure time. However, the total surface area of the resin sample sulfonated in the rotating drum reactor was approximately 153 times greater than the surface area of polypropylene film samples sulfonated in earlier studies (Asthana, 1993 and Wangwiwatsilp, 1993). A clog or blockage within the SO_3 synthesizer system, as found after completion of these studies, could have retarded the production of SO_3, resulting in a low molar concentration of SO_3 available for sulfonation process. The marked increase in the surface area of the resin sample, together with the clogging of the SO_3 synthesizer, may have led to a depletion of SO_3 gas and a

concomitant reduction in reaction rate following a 10 minute exposure time.

3. The increase in the polar characteristic of polypropylene resin, at the low sulfonation level achieved, was not sufficient to substantially improve the interfacial interaction between fibers and matrix, and therefore a minimal effect on the enhancement of mechanical properties, to include tensile properties, flexural properties and Izod impact strength, was observed.

4. All composites stored under humidified conditions exhibited water sorption, with the extent of water sorbed increasing with increased storage time up to 7 to 9 weeks, at which time the equilibrium sorption level was achieved. The maximum weight increase was approximately 2.2 to 2.5 % by weight. The sample water sorption was attributed mainly to the presence of the wood fibers, which are hydrophilic in nature. Even though the composites experienced water uptake during storage, no change in the tensile strength of the composite samples was found with an increase in storage time.

5. Polymer surface sulfonation was found to have no statistically significant effect on the water sorption capacity of the composites. Moreover, the physical properties of composites were relatively unaffected by the sulfonation. These findings are assumed to result from the low sulfonation level achieved on the sulfonated PP resin.

6. At the sulfonation levels achieved in the present study, there is some evidence indicating that sulfonation had a positive effect on enhancing the mechanical properties of the resultant composite structures. For example, the observed increase in tensile strength and flexural strength of the sulfonated PP/wood-fiber composites as compared to those of their nonsulfonated counterparts. These enhanced mechanical property levels were not considered sufficient to find utility for such modified composites in a commercial or industrial practice, since the maximum achievement of the sulfonation step was still low. However, surface sulfonation of the polymer resin showed potential as a method for enhancing the mechanical properties of the composite system with wood fibers, assuming that a higher sulfonation level of the PP resin, as found with PP film samples, is achieved.

RECOMMENDATIONS FOR FURTHER RESEARCH

1. Because of the clogging problem found with the sulfur trioxide synthesizer, and the associated depletion of SO_3 concentration during the sulfonation reaction on PP resin samples, future studies should include repeating the sulfonation process after the SO_3 generator has been repaired. The operational parameters that were utilized in this study should be employed. Higher levels of sulfonation should be achieved with higher molar concentrations of SO_3 being generated by the synthesizer.

2. Since PP has been found to achieve higher sulfonation levels, up to approximately 9 propylene monomer units per one sulfonate group, or three times the level achieved in the present study, the limitation on the sulfonation of PP resin does not result from inherent characteristics of the polymer itself, but from some external factors such as the ratio of the resin surface area to SO_3 concentration, and a restriction of the total resin sample surface area exposed to the gaseous SO_3. Techniques or conditions that would control the external parameters of the sulfonation process should be considered in an attempt to optimize the process in achieving the maximum degree of sulfonation on the PP resin. For example, reducing further the amount of resin, or increasing the SO_3 concentration may be done, in order to decrease the ratio of resin surface area to SO_3

concentration. Those should be conducted simultaneously with the use of a well-agitated drum reactor. Therefore, collaboration with engineering personnel and technicians or operators might be necessary to achieve this end.

3. The compounding technique utilized for this study was done by feeding dry blends between PP powder and fibers to the feeding zone of the twin-screw extruder. A disadvantage of this technique is that the fibers are exposed to high shear forces during the melting of the polymer, thus damaging the fibers (Bigg, 1985). Further, the fibers are exposed to high temperatures for a period of time equal to the polymer residence time. The long residence time of the wood fibers in the extruder can result in fiber degradation and breakage, even though the processing heat was controlled at a lower level than its degradation temperature (~200 ^{o}C). This, in turn, will affect the mechanical properties of composites. Thus, the compounding technique should be done by adding fibers to the extruder at a point where the polymer has already been melted. This technique has been used by current researchers in the wood fibers/thermoplastic composite field and it was found to yield less fiber damage during the compounding process.

In order to achieve a sufficient modification of polar characteristics of the polypropylene resin structure and concomitant improvement of the mechanical properties of the composite system with wood fibers, the optimization of the sulfonation process and a careful selection of compounding technique are important steps for further research.

APPENDICES

APPENDIX A

Modulated Differential Scanning Calorimetry

Modulated differential scanning calorimetry (MDSC) is a new technique which measures differential heat flow between a sample of a material and inert reference at the same temperature. The temperature modulation is programmed to scan a temperature range at predetermined amplitude and period. Thus, the heat flow is determined as a function of sinusoidal change in temperature and as a function of linear change in temperature when average temperature change is utilized. As a result, MDSC give the same information as conventional differential scanning calorimetry (DSC) does, with additional information related to the material properties.

The raw signals from the MDSC method are (i) modulated heat flow; and (ii) modulated heating rate (or a derivative of temperature over time). Throughout the mathematical calculations, three curves of heat flow from the MDSC raw signals are evaluated:

1) Total heat flow. Total heat flow is defined as a sum of all thermal events in the sample and is acquired by averaging the modulated heat flow. This signal is equivalent to the signal received from the conventional DSC.

2) Reversing heat flow. Reversing heat flow is the heat capacity component of the total heat flow, and it is calculated by multiplying heat capacity (proportional to the ratio of the heat flow amplitude to heating rate amplitude) with the average heating rate.

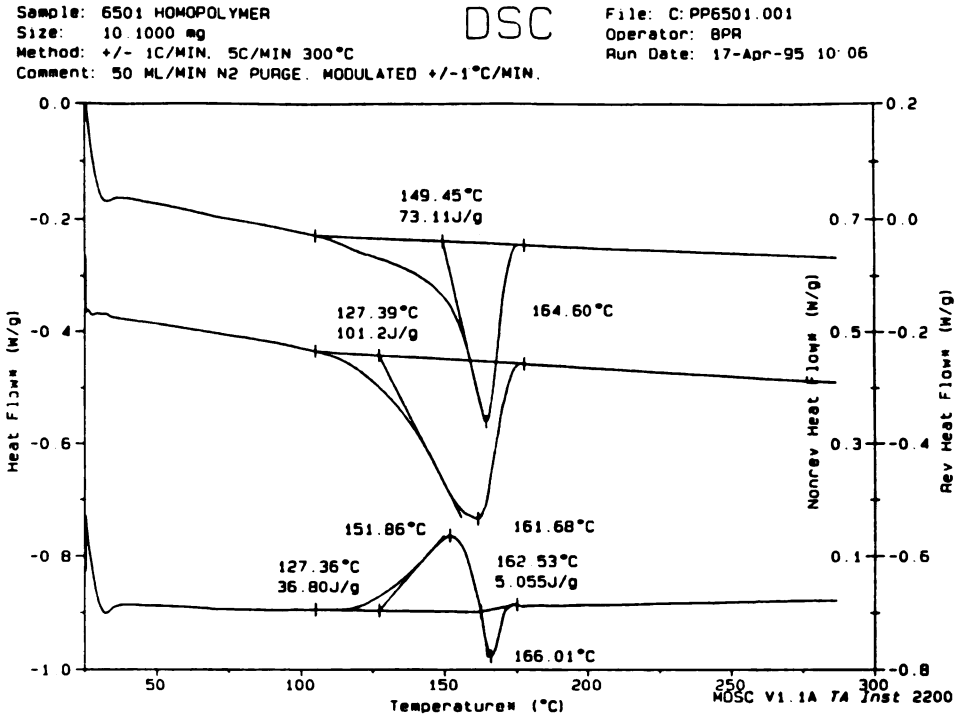
3) Nonreversing heat flow. It refers to the kinetic component of the total heat flow and is equal to the total heat flow signal subtracted by the reversing heat flow signal. The transitions occurring in the resultant signal are usually nonreversible at specified conditions, such as relaxation, cold crystallinity, decomposition, and thermoset cure.(Source: TA Instruments Co.)

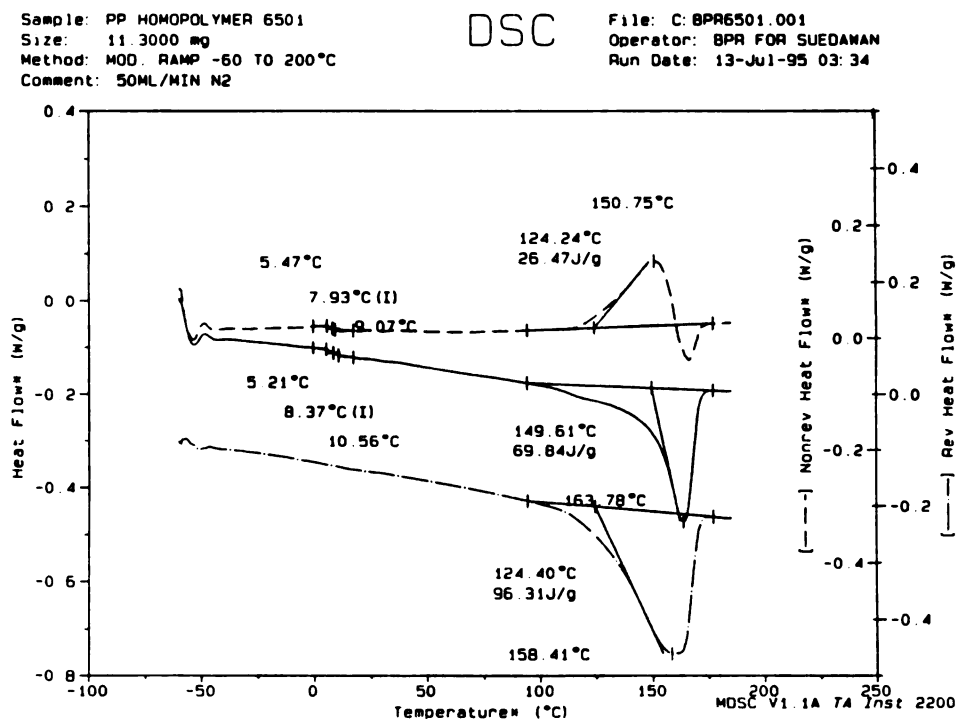
The melting temperature (Tm) and heat of fusion of polypropylene resin were obtained from the total heat flow curve. The percent crystallinity values of the resin were evaluated by the heat of fusion data of the sample examined in relation to the heat of fusion of the PP having 100 % crystallinity, of which the value is 209 J/g (Brandrup and Immergut, 1975). The melting temperature, heat of fusion and percent crystallinity of the PP resin were summarized in Table 14.

Table 14: Properties of PP Resin Determined by Modulated Differential Scanning Calorimeter

Sample No.	Melt Temp. (°C)	Heat of Fusion (J/g)	%Crystallinity
1	164.60	73.11	34.98
2	163.78	69.84	33.42
Mean	164.19	71.48	34.20
Sd.	0.58	2.31	1.10

Figure 16: MDSC Curves for PP Resin





APPENDIX B

ESCA Analysis

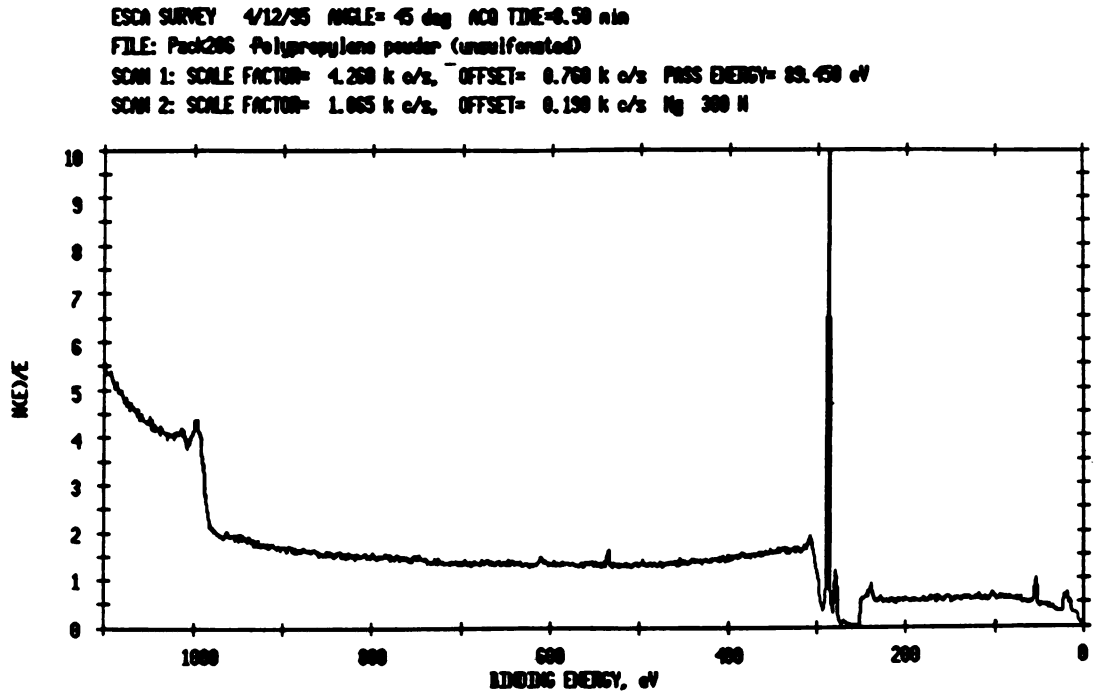


Figure 17: ESCA Analysis for Nonsulfonated PP Resin

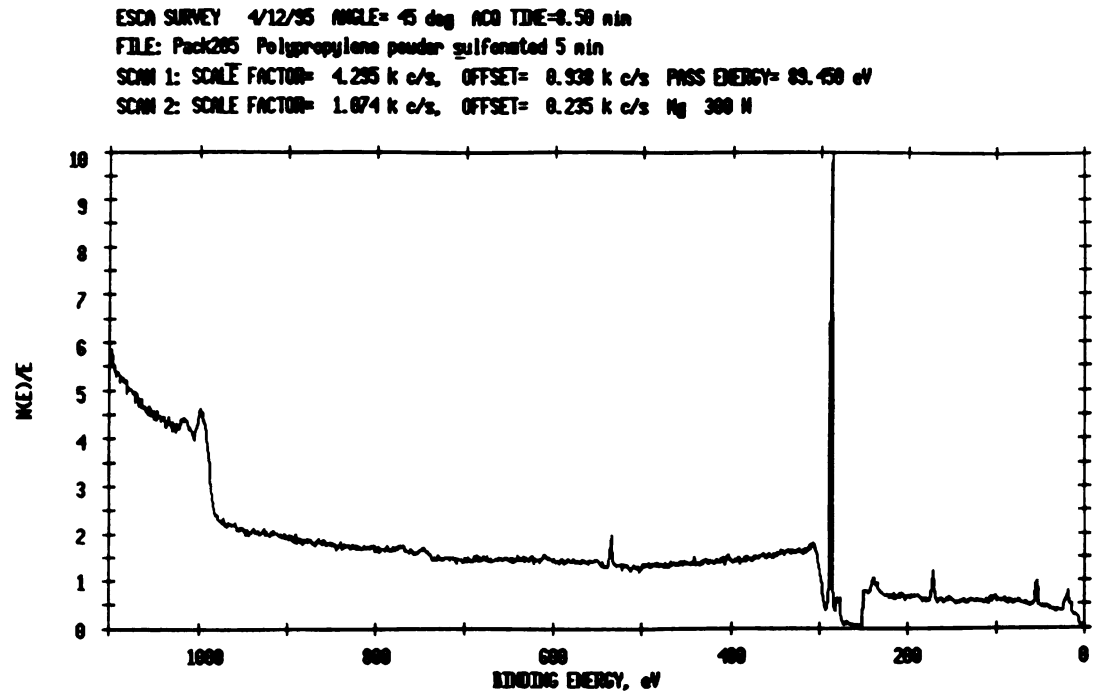


Figure 18: ESCA Analysis for 5-min Sulfonated PP Resin

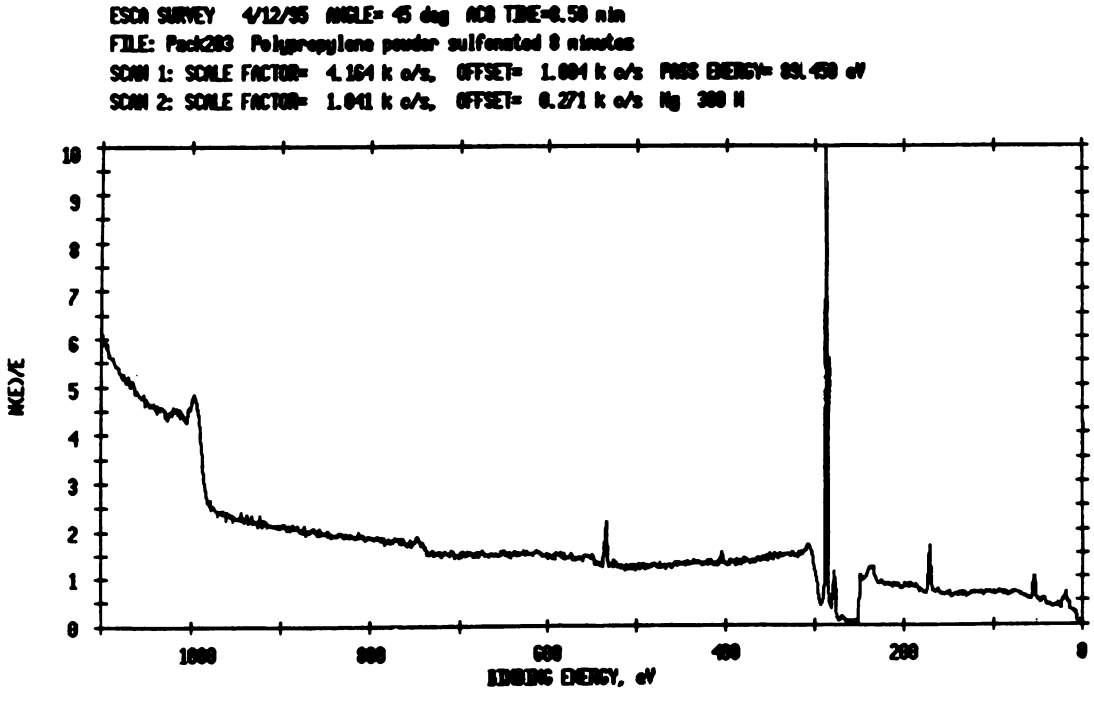


Figure 19: ESCA Analysis for 8-min Sulfonated PP Resin

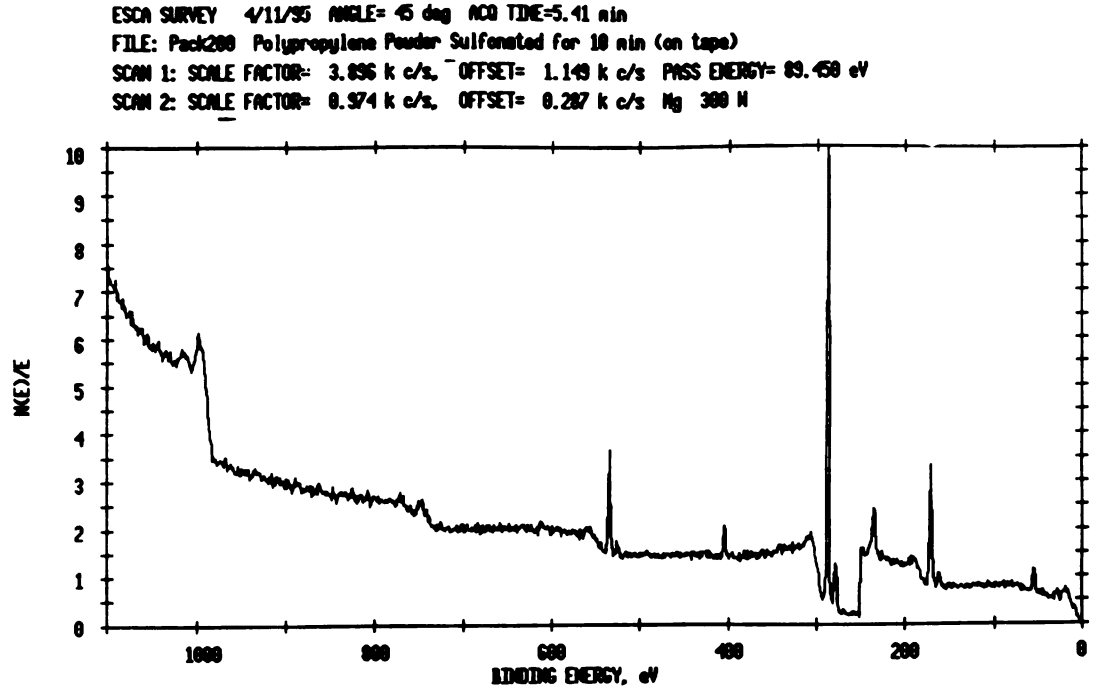


Figure 20: ESCA Analysis for 10-min Sulfonated PP Resin

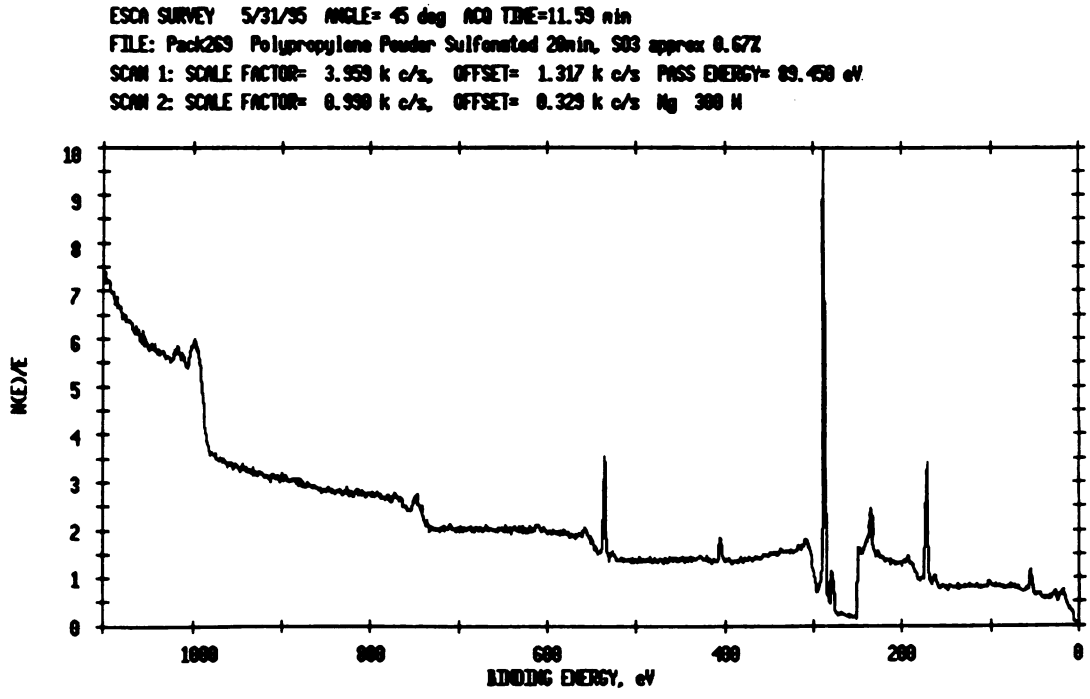


Figure 21: ESCA Analysis for 20-min Sulfonated PP Resin

APPENDIX C

Density Measurement

Table 15: Data of Density (g/cc)

Material	Replications				
	1	2	3	4	5
NS	1.055	1.069	1.058	1.029	1.040
	1.036	1.062	1.041		
NSn	1.052	1.018	1.042	1.085	1.045
	1.079	1.059	1.046	1.047	
S5	1.065	1.069	1.044	1.072	1.040
	1.063	1.029	1.028	1.070	1.048
S8	1.072	1.042	1.053	1.045	1.050
	1.048	1.048	1.045	1.063	1.034
S10	1.044	1.077	1.071	1.052	1.058
	1.057	1.064	1.073	1.075	1.074
S10n	1.041	1.075	1.043	1.075	1.055
	1.054	1.067	1.083	1.054	1.082
S20n	1.073	1.066	1.089	1.073	1.067
	1.078	1.082	1.090	1.085	

Mechanical Properties

Table 16: Data of Tensile Strength at Break (MPa)

Material	Replications						
	1	2	3	4	5	6	7
NS (LD)	15.77	16.66	17.33	15.96	17.14	16.86	17.73
	14.62	18.04	17.23	13.77	15.02	14.67	17.22
NS (CD)	18.32	15.66	16.27	17.61	15.62	15.21	12.97
	15.54	16.54	16.13	14.56	15.11	13.49	14.76
NSn (LD)	16.69	15.55	17.83	16.73	16.07	16.41	16.29
	16.67	14.96	17.75	16.98	17.26	14.79	
NSn (CD)	14.00	11.81	11.31	14.92	13.10	10.41	12.40
	14.76	14.13	15.76	14.55	13.00	13.39	
S5 (LD)	17.42	19.37	17.77	18.67	17.43	19.00	17.38
	21.13	18.96	18.79	19.58	21.69	19.28	21.91
S5 (CD)	18.73	16.33	21.24	22.04	20.60	21.84	20.14
	18.33	18.35	15.25	17.26	17.40	16.91	16.20
S8 (LD)	15.32	19.06	18.50	19.11	18.60	18.50	18.18
	20.77	17.44	20.22	20.63	20.46	20.63	19.10
S8 (CD)	18.96	18.02	19.34	16.13	17.50	17.15	16.38
	17.90	18.38	20.20	17.34	17.78	17.38	19.68
S10 (LD)	14.20	21.13	18.49	21.46	18.69	18.30	20.73
	18.60	19.28	17.60	17.23	18.51	18.55	19.64
S10 (CD)	17.80	17.78	16.88	16.73	17.82	16.62	16.48
	16.38	13.60	15.80	20.14	20.35	17.27	16.10
S10n (LD)	18.38	18.04	16.62	17.64	18.00	15.93	17.90
	15.70	19.28	20.88	16.68	17.80	19.02	
S10n (CD)	19.71	14.91	19.24	14.45	12.49	19.40	14.27
	13.81	17.13	17.37	15.43	15.77	14.11	
S20n (LD)	19.64	19.01	18.94	20.46	20.24	21.22	18.78
	19.44	16.56	18.40	19.90	19.32	19.12	
S20n (CD)	18.69	20.21	19.09	17.92	18.95	18.91	15.36
	17.13	21.40	21.28	19.26	20.64	20.09	
PP[a]	33.90	33.10	33.03	33.61	33.37	33.26	33.46
	33.54	33.15	33.03	33.04	33.20	33.28	33.50

[a] Reported as tensile strength at yield

Table 17: Data of Percent Elongation at Break

Material	Replications						
	1	2	3	4	5	6	7
NS (LD)	1.00	3.22	4.59	4.29	1.73	4.35	3.65
	3.59	2.68	1.52	2.13	2.72	2.47	2.67
NS (CD)	1.93	2.45	2.88	1.79	1.53	2.65	1.08
	1.42	1.59	1.03	1.62	0.10	1.90	
NSn (LD)	4.75	5.66	3.23	5.59	4.04	4.78	5.43
	3.05	5.35	4.66	3.91	4.29	6.81	3.84
NSn (CD)	2.73	2.13	1.50	2.45	2.56	2.07	2.22
	3.80	2.78	1.72	3.05	2.46	2.60	1.40
S5 (LD)	1.20	2.11	1.21	0.92	0.93	1.26	1.13
	1.36	1.74	1.30	2.36	1.88	1.15	
S5 (CD)	0.75	0.73	1.09	1.15	1.40	1.55	1.44
	1.33	1.27	0.63	1.09	1.02	0.88	0.93
S8 (LD)	0.77	1.07	1.14	1.19	1.32	1.31	1.29
	1.54	1.29	1.59	1.59	1.84	1.67	1.23
S8 (CD)	1.82	1.21	1.72	1.29	1.18	1.27	0.98
	1.68	0.92	1.60	1.10	0.98	0.98	1.60
S10 (LD)	0.57	2.12	1.40	1.73	1.49	1.55	1.72
	1.85	2.29	1.61	1.54	2.39	1.58	2.23
S10 (CD)	1.50	0.89	1.25	1.77	1.15	1.59	0.96
	0.83	0.95	2.98	1.52	0.81	0.73	
S10n (LD)	2.00	1.85	1.89	3.17	2.09	1.41	1.95
	3.07	1.67	3.02	2.69	1.52	2.32	3.00
S10n (CD)	2.20	1.44	2.01	1.57	1.02	2.45	1.24
	2.11	1.60	2.44	2.69	2.35	2.37	1.63
S20n (LD)	1.29	2.07	1.66	2.11	1.66	1.85	1.84
	2.03	1.87	1.03	1.65	1.83	2.02	1.64
S20n (CD)	1.87	2.23	1.45	1.26	1.59	1.93	0.89
	1.88	1.63	2.03	1.84	2.02	1.54	1.84
PP[a]	9.36	7.99	9.03	9.08	8.97	8.97	8.74
	8.84	8.93	8.93	9.17	8.36	8.51	9.06

[a] Reported as percent elongtion at yield

Table 18: Data of Modulus of Elasticity (MPa)

Material	Replications						
	1	2	3	4	5	6	7
NS (LD)	2930	2618	3241	3354	3912	3478	3048
	3724	2921	3437	3389	3058	3415	3409
NS (CD)	2921	2839	3143	3461	3268	3102	2982
	2655	3336	2981	3249	3519	2682	
NSn (LD)	2664	3295	2695	3479	2862	3590	2198
	2770	2566	3084	2752	2617	2834	2576
NSn (CD)	3059	2212	3312	1846	2313	2230	2740
	2406	2095	1992	3123	2835	2247	
S5 (LD)	3779	4061	3736	3547	4385	3930	2848
	2807	2788	3068	2706	2760	3889	
S5 (CD)	2795	2723	3229	3526	3652	2966	2832
	2132	4356	3232	2927	2917	3302	
S8 (LD)	3385	3163	3154	3287	3969	3221	2963
	3452	4346	3771	2853	3802	3510	3732
S8 (CD)	3912	4304	3945	4006	4059	3301	2824
	2921	3478	3093	3215	3269	3006	
S10 (LD)	3254	3225	3763	3047	3257	2977	3410
	2496	2737	2805	2545	2441	2972	3142
S10 (CD)	2755	3336	3265	3621	3476	3626	3525
	2839	2106	2495	2588	2440	3371	
S10n (LD)	2981	2758	2686	2795	2657	2661	3056
	2762	2717	2553	2753	3011	2748	
S10n (CD)	2595	3138	2877	2761	2067	2963	2985
	2832	3306	2597	3130	2597	3130	2849
S20n (LD)	2615	3128	2142	3562	3189	2624	2737
	2493	2730	3607	3165	2755	3299	
S20n (CD)	3456	2205	3467	2479	2852	2647	2821
	2282	3072	2730	2783	2884	3030	
PP	2215	1705	1624	1717	1788	1684	1697
	1616	1933	1669	1672	1735	1649	1449

Table 19: Data of Flexural Strength (MPa)

Material	Replications							
	1	2	3	4	5	6	7	8
NS (LD)	39.01	39.32	34.21	41.39	44.52	34.38	40.93	35.90
	42.86	40.38	36.69	38.13	36.49	42.07	36.15	34.25
NS (CD)	33.25	31.00	31.41	34.48	33.12	36.51	36.91	35.62
	43.08	44.23	41.86	39.32	42.75	36.88	38.34	38.97
NSn (LD)	38.34	40.70	38.33	41.02	40.65	39.06	40.03	45.84
	43.93	36.47	42.75	38.35	39.34	44.69	40.23	36.72
NSn (CD)	43.26	26.59	37.01	35.75	36.96	30.40	27.60	40.33
	35.99	36.85	31.57	35.30	35.52	32.05	35.87	33.39
S5 (LD)	43.71	41.82	39.71	37.81	46.00	38.43		
	42.66	40.84	40.10	41.98	42.36	45.42		
S5 (CD)	38.04	42.53	39.29	36.89	40.55	38.56	41.80	35.10
	43.27	34.73	45.32	33.65	41.62	39.74	39.82	43.84
S8 (LD)	32.58	39.83	39.40	38.26	38.52	36.47	34.47	35.46
	43.00	43.99	43.47	42.34	42.60	42.67	44.60	43.21
S8 (CD)	37.02	41.22	42.45	42.29	40.20	35.74	33.64	43.73
	41.91	40.83	40.69	40.82	40.84	40.71	40.00	42.26
S10 (LD)	44.51	39.80	43.36	45.78	39.94	45.71	37.58	41.25
	49.44	44.01	45.33	38.60	43.43	38.15	46.27	38.10
S10 (CD)	36.85	42.47	42.09	41.25	43.85	43.60	38.58	39.26
	32.68	38.93	43.33	33.35	39.32	36.55	40.84	36.78
S10n (LD)	47.35	37.16	38.10	44.30	45.79	41.91	40.52	44.55
	45.16	38.43	44.43	39.29	46.22	41.65	45.99	38.96
S10n (CD)	35.98	29.74	39.41	40.09	44.49	41.96	40.45	41.08
	41.96	43.23	43.81	43.81	41.91	40.52	43.80	44.18
S20n (LD)	40.29	41.05	37.80	42.19	38.67	44.52	40.11	42.70
	39.36	40.59	45.85	39.89	42.81	38.25	44.87	45.13
S20n (CD)	44.35	44.49	38.07	44.62	30.70	44.46	43.71	44.34
	44.04	45.60	43.77	43.60	48.18	41.58	43.49	47.49

Table 20: Data of Flexural Modulus (MPa)

Material	Replications							
	1	2	3	4	5	6	7	8
NS (LD)	2993	3393	2953	2784	3473	3259	2990	2914
	3111	2985	2879	2822	3113	2938	2855	2809
NS (CD)	2482	2486	2288	2623	2826	2586	2488	2582
	2828	3217	3050	2857	3029	2705	2643	2811
NSn (LD)	1858	2750	2224	2847	2442	2536	2470	2481
	2831	2627	2860	2565	2351	3100	3082	2733
NSn (CD)	2568	2100	2354	2226	2406	2511	2180	2323
	2441	2328	2187	2415	2388	2475	2562	2525
S5 (LD)	3102	2976	2846	2996	3263	2924		
	3093	2882	2955	2983	2953	2969		
S5 (CD)	3092	2958	3403	2766	3013	2955	3177	
	3280	3064	3029	3150	3093	3269		
S8 (LD)	2681	2826	2706	2783	3006	2657	2871	2597
	3106	3131	3282	3022	2938	3107	3073	3050
S8 (CD)	2826	3130	2986	2994	2875	2760	2331	3234
	3003	2841	2904	3002	3112	2558	2822	3023
S10 (LD)	3196	2905	2824	2858	2981	3253	3166	2805
	3188	2934	3236	2872	2905	2943	2997	2768
S10 (CD)	2683	2924	2785	2756	2994	2887	2745	2854
	2626	2965	2753	2447	3108	2805	2979	2852
S10n (LD)	3050	2713	2626	2990	2613	2695	2894	2951
	3192	2717	2925	2811	2888	2792	2736	2597
S10n (CD)	2433	2434	2778	2691	2840	2905	2821	2722
	2722	2828	2732	2715	2766	2498	2638	2793
S20n (LD)	2603	2734	2419	2897	2510	2871	2460	2865
	2763	3017	2457	2604	2799	2755	2997	2766
S20n (CD)	2722	2905	2728	2866	2426	2772	2938	2796
	2503	2842	2810	2557	3126	2773	2897	3134
PP	1367	1499	1895	1440	1384	1363	1479	
	1392	1507	1309	1410	1492	1415	1404	

Table 21: Data of Izod Impact Strength (J/m)

Material	Replications							
	1	2	3	4	5	6	7	8
NS (LD)	20.02	23.49	20.39	21.67	20.55	19.70	17.88	20.39
	20.02	21.46	18.31	19.86	26.32	20.71	18.63	21.03
NS (CD)	22.05	22.26	21.89	22.21	23.65	23.49	24.45	22.21
	22.05	23.49	23.49	22.05	21.89	21.67	22.05	21.67
NSn (LD)	30.64	35.82	30.64	34.22	32.94	30.86	36.41	36.68
	31.87	30.86	38.17	32.03	29.84	33.05	34.49	33.58
NSn (CD)	35.00	32.07	32.55	33.00	29.95	37.85	33.05	34.25
	36.35	34.98	35.31	37.97	36.50	32.25	38.56	30.06
S5 (LD)	21.73	19.22	21.51	21.03	22.42	18.26	21.67	22.26
	21.19	19.38	19.54	20.39	21.51	18.63	20.39	21.67
S5 (CD)	19.70	23.65	21.51	23.49	21.03	21.67	20.15	19.54
	21.67	18.52	18.52	20.23	19.70	19.86	18.31	19.70
S8 (LD)	25.52	20.34	24.45	22.42	20.02	24.45	20.34	23.38
	18.95	20.39	20.39	20.71	20.39	20.02	24.66	19.11
S8 (CD)	19.54	19.54	19.70	19.70	21.19	20.02	17.72	19.54
	21.09	20.39	20.71	18.95	20.02	19.27	20.87	18.63
S10 (LD)	26.80	19.91	25.95	28.24	25.57	24.29	24.29	21.19
	26.16	25.41	25.57	28.72	29.90	34.17	29.42	31.12
S10 (CD)	23.12	27.65	29.04	24.29	25.04	24.50	25.25	27.23
	25.47	24.08	25.68	22.21	19.11	22.05	19.70	21.89
S10n (LD)	21.19	22.05	23.12	20.39	23.12	26.32	27.44	21.67
	26.37	25.47	29.42	26.59	25.04	24.45	23.54	26.37
S10n (CD)	27.39	26.96	27.17	27.39	24.08	23.65	25.47	24.08
	24.17	24.82	25.47	25.47	23.49	25.47	25.63	25.63
S20n (LD)	21.19	25.04	21.19	20.66	24.29	20.82	22.74	19.22
	22.58	19.38	21.51	19.54	21.51	23.12	19.91	18.95
S20n (CD)	20.66	18.95	20.82	19.38	19.22	19.22	22.74	20.98
	17.46	20.71	18.95	17.46	17.03	17.19	18.95	18.79
PP	19.33	19.11	20.98	30.38	20.82	20.34	18.95	21.51
	17.56	17.03	17.56	21.09	19.07	23.12	18.79	22.21

APPENDIX D

Water Sorption Studies

Table 22: Data of Weight (gram) Measured At Different Periods of Storage Time

(1) Nonsulfonated Composite (NS)

Replications	Storage Time					
	0-week	1-week	3-week	5-week	7-week	9-week
1	6.0906	6.1517	6.1937	6.2212	6.2438	6.2432
2	6.0761	6.1340	6.1741	6.2008	6.2213	6.2213
3	6.5440	6.6100	6.6554	6.6862	6.7110	6.7108
4	6.4253	6.5010	6.5515	6.5868	6.6127	6.6110
5	6.2861	6.3417	6.3790	6.4047	6.4245	6.4272
6	6.0410	6.1018	6.1419	6.1693	6.1911	6.1930
7	6.0583	6.1167	6.1563	6.1836	6.2033	6.2052
8	6.2035	6.2662	6.3079	6.3356	6.3578	
9	6.1895	6.2443	6.2823	6.3080	6.3276	
10	6.3592	6.4298	6.4770	6.5077	6.5330	
11	6.2465	6.3164	6.3639	6.3958	6.4204	
12	5.9360	5.9926	6.0313	6.0570	6.0771	
13	6.2775	6.3379	6.3788	6.4068	6.4285	
14	6.0421	6.1025	6.1430	6.1705	6.1920	
15	6.4207	6.4909	6.5380	6.5705		
16	6.8378	6.9176	6.9741	7.0128		
17	6.3910	6.4544	6.4977	6.5272		
18	6.2788	6.3383	6.3788	6.4061		
19	6.2489	6.3063	6.3448	6.3717		
20	6.3366	6.3987	6.4410	6.4704		
21	6.2465	6.3219	6.3716	6.4063		
22	6.2538	6.3297	6.3786			
23	6.2216	6.2950	6.3446			
24	6.5055	6.5718	6.6160			
25	6.2697	6.3268	6.3662			
26	6.2767	6.3338	6.3729			
27	6.0933	6.1514	6.1914			

(2) 5-min Sulfonated Composite (S5)

Replications	Storage Time					
	0-week	1-week	3-week	5-week	7-week	9-week
1	6.0010	6.0319	6.0678	6.0916	6.1103	6.1110
2	6.0093	6.0637	6.0990	6.1237	6.1427	6.1443
3	6.1869	6.2392	6.2741	6.2979	6.3170	6.3185
4	5.9342	5.9858	6.0190	6.0418	6.0595	6.0604
5	6.0876	6.1419	6.1779	6.2025	6.2218	6.2230
6	6.1608	6.2141	6.2488	6.2735	6.2920	6.2941
7	5.9147	5.9655	5.9991	6.0224	6.0390	6.0407
8	6.2261	6.2855	6.3230	6.3493	6.3693	
9	6.0847	6.1413	6.1777	6.2034	6.2221	
10	6.2446	6.3051	6.3435	6.3714	6.3921	
11	6.4730	6.5381	6.5805	6.6112	6.6339	
12	6.0179	6.0713	6.1064	6.1317	6.1504	
13	6.0783	6.1380	6.1765	6.2040	6.2242	
14	6.0458	6.1048	6.1428	6.1693	6.1892	
15	6.3256	6.3807	6.4169	6.4425		
16	6.1024	6.1614	6.2013	6.2289		
17	6.3000	6.3654	6.4081	6.4388		
18	6.5018	6.5591	6.5962	6.6231		
19	6.1107	6.1587	6.1900	6.2125		
20	6.0800	6.1409	6.1804	6.2075		
21	6.0699	6.1265	6.1620			
22	6.2542	6.3172	6.3580			
23	6.3412	6.4013	6.4402			
24	6.3292	6.3889	6.4280			
25	6.1843	6.2348	6.2672			
26	6.2841	6.3393	6.3759			
27	5.9759	6.0225	6.0530			

(3) 8-min Sulfonated Composite (S8)

Replications	Storage Time					
	0-week	1-week	3-week	5-week	7-week	9-week
1	6.2813	6.3409	6.3813	6.4100	6.4316	6.4335
2	5.9230	5.9870	6.0288	6.0577	6.0796	6.0803
3	5.9024	5.9654	6.0059	6.0342	6.0550	6.0560
4	6.2556	6.3134	6.3503	6.3780	6.3982	6.4015
5	6.3635	6.4221	6.4611	6.4875	6.5080	6.5112
6	6.3500	6.4080	6.4468	6.4739	6.4944	6.4979
7	5.9098	5.9587	5.9889	6.0103	6.0266	6.0288
8	6.0521	6.1128	6.1523	6.1800	6.2003	
9	6.2403	6.2957	6.3324	6.3590	6.3782	
10	6.0763	6.1313	6.1660	6.1923	6.2116	
11	6.2480	6.3079	6.3480	6.3758	6.3967	
12	6.0398	6.0885	6.1192	6.1412	6.1577	
13	6.2629	6.3100	6.3417	6.3640	6.3803	
14	6.1415	6.2004	6.2379	6.2655	6.2844	
15	6.2633	6.3117	6.3420	6.3647		
16	6.2233	6.2853	6.3253	6.3550		
17	5.9870	6.0435	6.0804	6.1069		
18	6.2974	6.3556	6.3935	6.4216		
19	6.1140	6.1681	6.2041	6.2294		
20	5.9910	6.0495	6.0878	6.1154		
21	6.5195	6.5823	6.6233	6.6526		
22	6.1674	6.2272	6.2681			
23	6.1217	6.1773	6.2154			
24	6.1023	6.1672	6.2088			
25	6.3048	6.3633	6.4023			
26	6.3557	6.4145	6.4541			
27	6.1514	6.2129	6.2538			
28	6.0586	6.1116	6.1486			

(4) 10-min Sulfonated Composite (S10)

Replications	Storage Time					
	0-week	1-week	3-week	5-week	7-week	9-week
1	6.5070	6.5803	6.6248	6.6514	6.6698	6.6687
2	6.3915	6.4615	6.5037	6.5285	6.5463	6.5440
3	6.5896	6.6595	6.7035	6.7291	6.7483	6.7473
4	6.1678	6.2263	6.2632	6.2871	6.3036	6.3050
5	6.4063	6.4796	6.5231	6.5499	6.5692	6.5668
6	6.4013	6.4727	6.5173	6.5489	6.5723	6.5767
7	6.4526	6.5317	6.5764	6.6022	6.6191	6.6159
8	6.0900	6.1473	6.1839	6.2084	6.2256	
9	6.6830	6.7527	6.7946	6.8218	6.8407	
10	6.8124	6.8890	6.9381	6.9732	6.9995	
11	6.3158	6.3897	6.4324	6.4577	6.4745	
12	6.1092	6.1679	6.2044	6.2283	6.2461	
13	6.4085	6.4784	6.5218	6.5484	6.5659	
14	6.5410	6.6166	6.6644	6.6985	6.7236	
15	6.2873	6.3660	6.4125	6.4385		
16	6.6730	6.7425	6.7861	6.8137		
17	6.4914	6.5612	6.6046	6.6304		
18	6.4502	6.5129	6.5537	6.5790		
19	6.3881	6.4581	6.5018	6.5279		
20	6.4860	6.5637	6.6094	6.6364		
21	6.5246	6.5962	6.6413	6.6727		
22	6.8015	6.8810	6.9314			
23	6.2062	6.2689	6.3089			
24	6.3235	6.3812	6.4182			
25	6.3150	6.3823	6.4254			
26	6.3410	6.4133	6.4571			
27	6.4272	6.4998	6.5481			
28	6.4993	6.5618	6.6015			

(5) Polypropylene (PP)

Replications	Storage Time					
	0-week	1-week	3-week	5-week	7-week	9-week
1	4.9072	4.9050	4.9044	4.9052	4.9037	4.9052
2	4.9791	4.9756	4.9755	4.9797	4.9758	4.9781
3	5.0060	5.0025	5.0025	5.0024	5.0029	5.0036
4	5.1055	5.1015	5.1016	5.1041	5.1019	5.1020
5	4.9510	4.9467	4.9466	4.9462	4.9466	4.9465
6	4.7381	4.7328	4.7332	4.7329	4.7328	4.7346
7	4.9540	4.9512	4.9510	4.9508	4.9507	4.9509
8	4.7261	4.7220	4.7223	4.7219	4.7224	
9	4.8114	4.8077	4.8080	4.8079	4.8079	
10	4.9870	4.9825	4.9824	4.9825	4.9823	
11	4.9175	4.9134	4.9133	4.9128	4.9129	
12	4.7848	4.7813	4.7808	4.7808	4.7809	
13	4.7872	4.7835	4.7830	4.7845	4.7838	
14	4.8271	4.8238	4.8228	4.8228		
15	4.9742	4.9704	4.9710	4.9698		
16	4.6509	4.6470	4.6467	4.6480		
17	4.5807	4.5773	4.5773	4.5769		
18	4.8224	4.8193	4.8181	4.8175		
19	4.6152	4.6120	4.6112	4.6112		
20	4.8994	4.8958	4.8958			
21	4.6940	4.6898	4.6902			
22	4.8678	4.8640	4.8640			
23	4.5773	4.5734	4.5735			
24	4.6348	4.6315	4.6315			
25	4.7038	4.7006	4.7003			

Table 23: Data of Tensile Strength (MPa) Measured After Different Periods of Storage Time

Material	Replications						
	1	2	3	4	5	6	7
After 3-week Storage							
NS	16.79	18.40	17.23	16.38	15.47	16.71	16.37
S5	17.45	18.52	16.78	16.22	21.02	19.58	20.23
S8	18.20	19.02	16.41	18.73	16.73	20.25	16.57
S10	20.16	18.92	18.46	20.87	15.87	18.85	
PP	35.22	36.03	35.65	35.35	34.95		
After 5-week Storage							
NS	16.55	13.45	16.13	18.75	15.03	16.58	19.01
S5	19.17	18.02	18.83	18.79	19.60	16.91	
S8	19.66	17.31	18.54	21.14	19.56	16.47	16.83
S10	18.76	19.06	15.36	19.27			
PP	33.48	33.36	33.67	33.23	34.05	33.56	
After 7-week Storage							
NS	16.78	16.82	17.38	15.42	16.20	15.59	14.90
S5	17.69	20.32	18.70	19.38	20.13	19.12	17.95
S8	16.63	18.48	16.42	19.23	19.17		
S10	20.55	16.33	18.21	17.40	19.28	16.74	19.01
PP	35.90	35.29	35.61	35.54	35.20	35.03	
After 9-week storage							
NS	16.20	17.70	17.35	14.27	19.26	14.81	15.02
S5	19.06	18.85	19.07	19.43	18.44		
S8	17.27	16.49	17.13	16.49	19.01	18.29	18.62
S10	16.67	17.43	17.42	19.39	17.06		
PP	34.70	34.05	34.23	34.28	34.49	34.69	

APPENDIX E

Statistical Analysis

Table 24: One-Way Analysis of Variance of Density Values

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	.0062	.0010	4.9907	.0003
Within Groups	59	.0123	.0002		
Total	65	.0185			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	8	1.0486	.0141	.0050	1.0367 TO 1.0604
NSn	9	1.0525	.0202	.0067	1.0369 TO 1.0680
S5	10	1.0529	.0170	.0054	1.0407 TO 1.0650
S8	10	1.0500	.0108	.0034	1.0422 TO 1.0577
S10	10	1.0644	.0114	.0036	1.0563 TO 1.0726
S10n	10	1.0629	.0155	.0049	1.0519 TO 1.0740
S20n	9	1.0783	.0090	.0030	1.0714 TO 1.0852
Total	66	1.0586	.0169	.0021	1.0544 TO 1.0627

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= .0102 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.32

	NS	S8	NSn	S5	S10n	S10	S20n
NS							
S8							
NSn							
S5							
S10n							
S10							
S20n	*	*	*	*			

(*) Indicates significant differences

Table 25: One-Way Analysis of Variance of Tensile Strength at Break Data, for Lengthwise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	134.9586	22.4931	11.3272	.0000
Within Groups	88	174.7470	1.9858		
Total	94	309.7056			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	14	16.2871	1.3274	.3548	15.5207 TO 17.0536
NSn	13	16.4600	.9430	.2616	15.8901 TO 17.0299
S5	14	19.1700	1.5100	.4036	18.2982 TO 20.0418
S8	14	19.0371	1.5034	.4018	18.1691 TO 19.9052
S10	14	18.7436	1.8130	.4845	17.6968 TO 19.7904
S10n	13	17.8362	1.4193	.3936	16.9785 TO 18.6938
S20n	13	19.3100	1.1271	.3126	18.6289 TO 19.9911
Total	95	18.1285	1.8151	.1862	17.7588 TO 18.4983

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= .9964 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.27

	NS	NSn	S10n	S10	S8	S5	S20n
NS							
NSn							
S10n							
S10	*	*					
S8	*	*					
S5	*	*					
S20n	*	*					

(*) Indicates significant differences

Table 26: One-Way Analysis of Variance of Tensile Strength at Break Data, for Crosswise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	324.2102	54.0350	17.2030	.0000
Within Groups	88	276.4098	3.1410		
Total	94	600.6200			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	14	15.5564	1.4299	.3822	14.7308 TO 16.3820
NSn	13	13.3492	1.5545	.4311	12.4099 TO 14.2886
S5	14	18.6157	2.2196	.5932	17.3341 TO 19.8973
S8	14	18.0100	1.1928	.3188	17.3213 TO 18.6987
S10	14	17.1250	1.6996	.4542	16.1437 TO 18.1063
S10n	13	16.0069	2.3563	.6535	14.5830 TO 17.4308
S20n	13	19.1485	1.6859	.4676	18.1297 TO 20.1673
Total	95	16.8512	2.5278	.2593	16.3362 TO 17.3661

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 1.2532 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.27

	NSn	NS	S10n	S10	S8	S5	S20n
NSn							
Ns	*						
S10n	*						
S10	*						
S8	*	*					
S5	*	*	*				
S20n	*	*	*				

(*) Indicates significant differences

Table 27: One-Way Analysis of Variance of Tensile Strength at Break Data in Lengthwise Direction Vs. Crosswise Direction

(1)Nonsulfonated PP Composite of Fiber-1 (NS)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	3.7376	3.7376	1.9637	.1729
Within Groups	26	49.4876	1.9034		
Total	27	53.2252			

(2)Nonsulfonated PP Composite of Fiber-2 (NSn)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	62.8998	62.8998	38.0541	.0000
Within Groups	24	39.6697	1.6529		
Total	25	102.5694			

(3)5-min Sulfonated PP Composite of Fiber-1 (S5)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	2.1506	2.1506	.5968	.4468
Within Groups	26	93.6897	3.6035		
Total	27	95.8404			

(4)8-min Sulfonated PP Composite of Fiber-1 (S8)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	7.3852	7.3852	4.0106	.0557
Within Groups	26	47.8767	1.8414		
Total	27	55.2618			

(5)10-min Sulfonated PP Composite of Fiber-1 (S10)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	18.3384	18.3384	5.9389	.0220
Within Groups	26	80.2841	3.0878		
Total	27	98.6225			

(6)10-min Sulfonated PP Composite of Fiber-2 (S10n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	21.7496	21.7496	5.7490	.0246
Within Groups	24	90.7960	3.7832		
Total	25	112.5455			

(7)20-min Sulfonated PP Composite of Fiber-2 (S20n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	.1696	.1696	.0825	.7764
Within Groups	24	49.3530	2.0564		
Total	25	49.5226			

Table 28: One-Way Analysis of Variance of Percent Elongation at Break Data, for Lengthwise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	115.3145	19.2191	41.0458	.0000
Within Groups	90	42.1411	.4682		
Total	96	157.4556			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	14	2.9007	1.1034	.2949	2.2636 TO 3.5378
NSn	14	4.6707	1.0367	.2771	4.0722 TO 5.2693
S5	13	1.4269	.4524	.1255	1.1535 TO 1.7003
S8	14	1.3457	.2776	.0742	1.1854 TO 1.5060
S10	14	1.7193	.4626	.1236	1.4522 TO 1.9864
S10n	14	2.2607	.6148	.1643	1.9057 TO 2.6157
S20n	14	1.7536	.3026	.0809	1.5789 TO 1.9283
Total	97	2.3058	1.2807	.1300	2.0477 TO 2.5639

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= .4839 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.27

	S8	S5	S10	S20n	S10n	NS	NSn
S8							
S5							
S10							
S20n							
S10n	*	*					
NS	*	*	*	*			
NSn	*	*	*	*	*	*	

(*) Indicates significant differences

Table 29: One-Way Analysis of Variance of Percent elongation at Break Data, for Crosswise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	16.4832	2.7472	10.4036	.0000
Within Groups	89	23.5016	.2641		
Total	95	39.9848			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	13	1.6900	.7346	.2038	1.2461 TO 2.1339
NSn	14	2.3907	.6320	.1689	2.0258 TO 2.7556
S5	14	1.0900	.2849	.0761	.9255 TO 1.2545
S8	14	1.3093	.3144	.0840	1.1278 TO 1.4908
S10	13	1.3023	.6078	.1686	.9350 TO 1.6696
S10n	14	1.9371	.5160	.1379	1.6392 TO 2.2351
S20n	14	1.7143	.3506	.0937	1.5119 TO 1.9167
Total	96	1.6363	.6488	.0662	1.5048 TO 1.7677

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= .3634 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.27

	S5	S10	S8	NS	S20n	S10n	NSn
S5							
S10							
S8							
NS	*						
S20n	*						
S10n	*	*	*				
NSn	*	*	*	*	*		

(*) Indicates significant differences

Table 30: One-Way Analysis of Variance of Percent Elongation at Break Data in Lengthwise Direction Vs. Crosswise Direction

(1)Nonsulfonated PP Composite of Fiber-1 (NS)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	9.8808	9.8808	11.0758	.0027
Within Groups	25	22.3027	.8921		
Total	26	32.1835			

(2)Nonsulfonated PP Composite of Fiber-2 (NSn)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	36.3888	36.3888	49.3706	.0000
Within Groups	26	19.1634	.7371		
Total	27	55.5522			

(3)5-min Sulfonated PP Composite of Fiber-1 (S5)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	.7652	.7652	5.4478	.0279
Within Groups	25	3.5115	.1405		
Total	26	4.2767			

(4)8-min Sulfonated PP Composite of Fiber-1 (S8)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	.0093	.0093	.1056	.7478
Within Groups	26	2.2872	.0880		
Total	27	2.2965			

(5)10-min Sulfonated PP Composite of Fiber-1 (S10)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	1.1720	1.1720	4.0613	.0547
Within Groups	25	7.2145	.2886		
Total	26	8.3865			

(6)10-min Sulfonated PP Composite of Fiber-2 (S10n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	.7329	.7329	2.2751	.1435
Within Groups	26	8.3756	.3221		
Total	27	9.1085			

(7)20-min Sulfonated PP Composite of Fiber-2 (S20n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	.0108	.0108	.1008	.7535
Within Groups	26	2.7879	.1072		
Total	27	2.7987			

Table 31: One-Way Analysis of Variance of Modulus of Elasticity Data, for Lengthwise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	6309613.809	1051602.301	6.4980	.0000
Within Groups	88	14241449.41	161834.6524		
Total	94	20551063.22			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	14	3281.0000	340.4608	90.9920	3084.4238 TO 3477.5762
NSn	14	2855.8571	382.8729	102.3271	2634.7929 TO 3076.9214
S5	13	3408.0000	594.1968	164.8005	3048.9305 TO 3767.0695
S8	14	3472.0000	413.4537	110.5002	3233.2789 TO 3710.7211
S10	14	3005.0714	375.7557	100.4249	2788.1165 TO 3222.0263
S10n	13	2779.8462	148.9820	41.3202	2689.8172 TO 2869.8751
S20n	13	2926.6154	434.7339	120.5735	2663.9083 TO 3189.3225
Total	95	3106.1368	467.5771	47.9724	3010.8865 TO 3201.3872

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 284.4597 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.27

	S10n	NSn	S20n	S10	NS	S5	S8
S10n							
NSn							
S20n							
S10							
NS	*						
S5	*	*	*				
S8	*	*	*	*			

(*) Indicates significant differences

Table 32: One-Way Analsis of Variance of Modulus of Elasticity Data, for Crosswise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	7449904.231	1241650.705	6.5022	.0000
Within Groups	85	16231454.20	190958.2847		
Total	91	23681358.43			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	13	3087.5385	275.8069	76.4951	2920.8700 TO 254.2069
NSn	13	2493.0769	469.2742	130.1532	2209.4974 TO 776.6564
S5	13	3122.2308	536.7756	130.1532	2797.8606 TO 446.6010
S8	13	3487.1538	496.4146	137.6806	3187.1735 TO 787.1342
S10	13	3034.0769	517.1182	143.4228	2721.5855 TO 346.5683
S10n	14	2844.7857	315.4241	84.3006	2662.6653 TO 026.9061
S20n	13	2823.6923	382.8621	106.1868	2592.3311 TO 055.0536
Total	92	2983.1304	510.1320	53.1849	2877.4851 TO 088.7758

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 308.9970 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.27

	NSn	S20n	S10n	S10	NS	S5	S8
NSn							
S20n							
S10n							
S10	*						
NS	*						
S5	*						
S8	*	*	*				

(*) Indicates significant differences

Table 33: One-Way Analysis of Variance of Modulus of Elasticity Data in Lengthwise Direction Vs. Crosswise Direction

(1)Nonsulfonated PP Composite of Fiber-1 (NS)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	252288.1766	252288.1766	2.6066	.1190
Within Groups	25	2419709.231	96788.3692		
Total	26	2671997.407			

(2)Nonsulfonated PP Composite of Fiber-2 (NSn)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	887145.4367	887145.4367	4.8762	.0366
Within Groups	25	4548310.637	181932.4255		
Total	26	5435456.074			

(3)5-min Sulfonated PP Composite of Fiber-1 (S5)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	530816.3462	530816.3462	1.6557	.2105
Within Groups	25	7694374.308	320598.9295		
Total	26	8225190.654			

(4)8-min Sulfonated PP Composite of Fiber-1 (S8)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	1547.9373	1547.9373	.0075	.9318
Within Groups	25	5179401.692	207176.0677		
Total	26	5180949.630			

(5)10-min Sulfonated PP Composite of Fiber-1 (S10)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	5671.1113	5671.1113	.0281	.8682
Within Groups	25	5044435.852	201777.4341		
Total	26	5050106.963			

(6)10-min Sulfonated PP Composite of Fiber-2 (S10n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	28426.6913	28426.6913	.4556	.5059
Within Groups	25	1559748.049	62389.9220		
Total	26	1588174.741			

(7)20-min Sulfonated PP Composite of Fiber-2 (S20n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	68855.5385	68855.5385	.4104	.5279
Within Groups	24	4026923.846	167788.4936		
Total	25	4095779.385			

Table 34: One-Way Analysis of Variance of Flexural Strength Data, for Lengthwise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	202.5037	33.7506	3.3503	.0047
Within Groups	101	1017.4535	10.0738		
Total	107	1219.9572			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	16	38.5425	3.2646	.8162	36.8029 TO 40.2821
NSn	16	40.4031	2.7242	.6811	38.9515 TO 41.8548
S5	12	41.7367	2.5386	.7328	40.1237 TO 43.3496
S8	16	40.0544	3.7600	.9400	38.0508 TO 42.0579
S10	16	42.5787	3.5812	.8953	40.6704 TO 44.4871
S10n	16	42.4881	3.3751	.8438	40.6896 TO 44.2866
S20n	16	41.5050	2.5829	.6457	40.1287 TO 42.8813
Total	108	41.0184	3.3766	.3249	40.3743 TO 41.6625

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 2.2443 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.26

	NS	S8	NSn	S20n	S5	S10n	S10
NS							
S8							
NSn							
S20n							
S5							
S10n	*						
S10	*						

(*) Indicates significant differences

Table 35: One-Way Analysis of Variance of Flexural Strength Data, for Crosswise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	723.8900	120.6483	8.7489	.0000
Within Groups	105	1447.9593	13.7901		
Total	111	2171.8493			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	16	37.3581	4.1618	1.0405	35.1404 TO 39.5758
NSn	16	34.6525	4.3079	1.0770	32.3570 TO 36.9480
S5	16	39.6719	3.3949	.8487	37.8628 TO 41.4809
S8	16	40.2719	2.6430	.6608	38.8635 TO 41.6803
S10	16	39.3581	3.4563	.8641	37.5164 TO 41.1998
S10n	16	41.0262	3.7367	.9342	39.0351 TO 43.0174
S20n	16	43.2806	4.0289	1.0072	41.1338 TO 45.4275
Total	112	39.3742	4.4234	.4180	38.5460 TO 40.2024

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 2.6258 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.25

	NSn	NS	S10	S5	S8	S10n	S20n
NSn							
NS							
S10	*						
S5	*						
S8	*						
S10n	*						
S20n	*	*					

(*) Indicates significant differences

Table 36: One-Way Analysis of Variance of Flexural Strength Data in Lengthwise Direction Vs. Crosswise Direction

(1)Nonsulfonated PP Composite of Fiber-1 (NS)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	11.2220	11.2220	.8022	.3776
Within Groups	30	419.6771	13.9892		
Total	31	430.8991			

(2)Nonsulfonated PP Composite of Fiber-2 (NSn)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	264.5575	264.5575	20.3664	.0001
Within Groups	30	389.6972	12.9899		
Total	31	654.2547			

(3)5-min Sulfonated PP Composite of Fiber-1 (S5)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	29.2345	29.2345	3.1181	.0892
Within Groups	26	243.7699	9.3758		
Total	27	273.0044			

(4)8-min Sulfonated PP Composite of Fiber-1 (S8)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	.3784	.3784	.0358	.8511
Within Groups	30	316.8446	10.5615		
Total	31	317.2231			

(5)10-min Sulfonated PP Composite of Fiber-1 (S10)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	82.9794	82.9794	6.6997	.0147
Within Groups	30	371.5644	12.3855		
Total	31	454.5438			

(6)10-min Sulfonated PP Composite of Fiber-2 (S10n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	17.0966	17.0966	1.3486	.2547
Within Groups	30	380.3144	12.6771		
Total	31	397.4110			

(7)20-min Sulfonated PP Composite of Fiber-2 (S20n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	25.2228	25.2228	2.2026	.1482
Within Groups	30	343.5451	11.4515		
Total	31	368.7678			

Table 37: One-Way Analysis of Variance of Flexural Modulus Data, for Lengthwise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	2287990.352	381331.7253	8.9892	.0000
Within Groups	101	4284554.167	42421.3284		
Total	107	6572544.519			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	16	3016.9375	204.9502	51.2376	2907.7272 TO 3126.1478
NSn	16	2609.8125	318.2199	79.5550	2440.2451 TO 2779.3799
S5	12	2995.1667	111.7764	32.2671	2924.1473 TO 3066.1860
S8	16	2927.2500	201.5181	50.3795	2819.8686 TO 3034.6314
S10	16	2989.4375	164.2425	41.0606	2901.9189 TO 3076.9561
S10n	16	2824.3750	170.0944	42.5236	2733.7381 TO 2915.0119
S20n	16	2719.8125	191.5436	47.8859	2617.7461 TO 2821.8789
Total	108	2864.2963	247.8420	23.8486	2817.0192 TO 2911.5734

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 145.6388 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.26

	NSn	S20n	S10n	S8	S10	S5	NS
NSn							
S20n							
S10n							
S8	*						
S10	*	*					
S5	*	*					
NS	*	*					

(*) Indicates significant differences

Table 38: One-Way Analysis of Variance of Flexural Modulus Data, for Crosswise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	4318995.674	719832.6123	20.8023	.0000
Within Groups	102	3529551.611	34603.4472		
Total	108	7848547.284			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	16	2718.8125	245.7273	61.4318	2587.8737 TO 2849.7513
NSn	16	2374.3125	143.0248	35.7562	2298.1000 TO 2450.5250
S5	13	3096.0769	165.2682	45.8372	2996.2064 TO 3195.9475
S8	16	2900.0625	221.7778	55.4445	2781.8854 TO 3018.2396
S10	16	2822.6875	160.8497	40.2124	2736.9767 TO 2908.3983
S10n	16	2707.2500	141.3952	35.3488	2631.9058 TO 2782.5942
S20n	16	2799.6875	193.8142	48.4536	2696.4112 TO 2902.9638
Total	109	2765.2661	269.5770	25.8208	2714.0848 TO 2816.4473

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 131.5360 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.25

	NSn	S10n	NS	S20n	S10	S8	S5
NSn							
S10n	*						
NS	*						
S20n	*						
S10	*						
S8	*						
S5	*	*	*	*	*		

(*) Indicates significant differences

Table 39: One-Way Analysis of Variance of Flexural Modulus Data in Lengthwise Direction Vs. Crosswise Direction

(1)Nonsulfonated PP Composite of Fiber-1 (NS)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	711028.1250	711028.1250	13.8891	.0008
Within Groups	30	1535797.375	51193.2458		
Total	31	2246825.500			

(2)Nonsulfonated PP Composite of Fiber-2 (NSn)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	443682.000	443682.0000	7.2902	.0113
Within Groups	30	1825799.875	60859.9958		
Total	31	2269481.875			

(3)5-min Sulfonated PP Composite of Fiber-1 (S5)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	63541.1703	63541.1703	3.1416	.0896
Within Groups	23	465196.5897	20225.9387		
Total	24	528737.7600			

(4)8-min Sulfonated PP Composite of Fiber-1 (S8)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	5913.2813	5913.2813	.1317	.7192
Within Groups	30	1346923.938	44897.4646		
Total	31	1352837.219			

(5)10-min Sulfonated PP Composite of Fiber-1 (S10)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	222444.500	222444.5000	8.4182	.0069
Within Groups	30	792723.375	26424.1125		
Total	31	1015167.875			

(6)10-min Sulfonated PP Composite of Fiber-2 (S10n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	109746.1250	109746.1250	4.4863	.0426
Within Groups	30	733870.7500	24462.3583		
Total	31	843616.8750			

(7)20-min Sulfonated PP Composite of Fiber-2 (S20n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	51040.125	51040.1250	1.3748	.2502
Within Groups	30	1113793.875	37126.4625		
Total	31	1164834.000			

Table 40: One-Way Analysis of Variance of Izod Impact Strength Data, for Lengthwise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	2048.9820	341.4970	60.6389	.0000
Within Groups	105	591.3228	5.6316		
Total	111	2640.3048			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	16	20.6519	2.0290	.5073	19.5707 TO 21.7331
NSn	16	33.2563	2.5213	.6303	31.9127 TO 34.5998
S5	16	20.6750	1.3088	.3272	19.9776 TO 21.3724
S8	16	21.5962	2.1816	.5454	20.4338 TO 22.7587
S10	16	26.6694	3.5831	.8958	24.7601 TO 28.5787
S10n	16	24.5344	2.5210	.6302	23.1910 TO 25.8777
S20n	16	21.3531	1.8115	.4529	20.3878 TO 22.3184
Total	112	24.1052	4.8771	.4608	23.1920 TO 25.0184

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 1.6780 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.25

	NS	S5	S20n	S8	S10n	S10	NSn
NS							
S5							
S20n							
S8							
S10n	*	*	*	*			
S10	*	*	*	*			
NSn	*	*	*	*	*	*	

(*) Indicates significant differences

Table 41: One-Way Analysis of Variance of Izod Impact Strength Data, for Crosswise Direction

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	6	2611.4955	435.2492	132.2490	.0000
Within Groups	105	345.5691	3.2911		
Total	111	2957.0646			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	16	22.5356	.8642	.2161	22.0751 TO 22.9961
NSn	16	34.3563	2.6780	.6695	32.9292 TO 35.7833
S5	16	20.4531	1.6114	.4029	19.5945 TO 21.3118
S8	16	19.8050	.9286	.2322	19.3102 TO 20.2998
S10	16	24.1444	2.7255	.6814	22.6920 TO 25.5967
S10n	16	25.3963	1.3078	.3270	24.6994 TO 26.0931
S20n	16	19.2819	1.5879	.3970	18.4357 TO 20.1280
Total	112	23.7104	5.1614	.4877	22.7439 TO 24.6768

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 1.2828 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 4.25

	S20n	S8	S5	NS	S10	S10n	NSn
S20n							
S8							
S5							
NS	*	*	*				
S10	*	*	*				
S10n	*	*	*	*			
NSn	*	*	*	*	*	*	

(*) Indicates significant differences

Table 42: One-Way Analysis of Variance of Izod Impact Strength Data in Lengthwise Direction Vs. Crosswise Direction

(1)Nonsulfonated PP Composite of Fiber-1 (NS)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	28.3881	28.3881	11.6733	.0018
Within Groups	30	72.9562	2.4319		
Total	31	101.3444			

(2)Nonsulfonated PP Composite of Fiber-2 (NSn)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	9.6800	9.6800	1.4310	.2410
Within Groups	30	202.9304	6.7643		
Total	31	212.6103			

(3)5-min Sulfonated PP Composite of Fiber-1 (S5)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	.3938	.3938	.1828	.6721
Within Groups	30	64.6447	2.1548		
Total	31	65.0386			

(4)8-min Sulfonated PP Composite of Fiber-1 (S8)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	25.6686	25.6686	9.1319	.0051
Within Groups	30	84.3258	2.8109		
Total	31	109.9944			

(5)10-min Sulfonated PP Composite of Fiber-1 (S10)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	51.0050	51.0050	5.0334	.0324
Within Groups	30	304.0017	10.1334		
Total	31	355.0067			

(6)10-min Sulfonated PP Composite of Fiber-2 (S10n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	5.9426	5.9426	1.4735	.2343
Within Groups	30	120.9870	4.0329		
Total	31	126.9296			

(7)20-min Sulfonated PP Composite of Fiber-2 (S20n)

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	1	34.3206	34.3206	11.8284	.0017
Within Groups	30	87.0462	2.9015		
Total	31	121.3668			

Table 43: One-Way Analysis of Variance of Tensile Strength Data Compared between Conditioned Samples, at a Period of Storage Time

(1) 3-Week Storage

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	17.1378	5.7126	2.5110	.0839
Within Groups	23	52.3252	2.2750		
Total	26	69.4630			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean		
NS	7	16.7643	.9013	.3407	15.9307	TO	17.5979
S5	7	18.5429	1.8146	.6859	16.8646	TO	20.2211
S8	7	17.9871	1.4640	.5534	16.6331	TO	19.3412
S10	6	18.8550	1.7224	.7032	17.0475	TO	20.6625
Total	27	18.0070	1.6345	.3146	17.3604	TO	18.6536

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 1.0665 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 3.91

- No two groups are significantly different at the .050 level

(2) 5-Week Storage

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	18.9657	6.3219	2.2755	.1110
Within Groups	20	55.5645	2.7782		
Total	23	74.5302			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	7	16.5000	1.9567	.7396	14.6904 TO 18.3096
S5	6	18.5533	.9585	.3913	17.5475 TO 19.5592
S8	7	18.5014	1.7208	.6504	16.9100 TO 20.0929
S10	4	18.1125	1.8469	.9234	15.1737 TO 21.0513
Total	24	17.8658	1.8001	.3674	17.1057 TO 18.6260

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 1.1786 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 3.95

- No two groups are significantly different at the .050 level

(3) 7-Week Storage

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	31.0640	10.3547	7.1320	.0016
Within Groups	22	31.9407	1.4519		
Total	25	63.0047			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	7	16.1557	.8916	.3370	15.3311 TO 16.9803
S5	7	19.0414	1.0062	.3803	18.1108 TO 19.9720
S8	5	17.9860	1.3679	.6117	16.2876 TO 19.6844
S10	7	18.2171	1.5062	.5693	16.8242 TO 19.6101
Total	26	17.8396	1.5875	.3113	17.1984 TO 18.4808

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= .8520 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 3.92

	NS	S8	S10	S5
NS				
S8				
S10	*			
S5	*			

(*) Indicates significant differences

(4) 9-Week Storage

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	19.8111	6.6037	4.2577	.0177
Within Groups	20	31.0202	1.5510		
Total	23	50.8313			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
NS	7	16.3729	1.8155	.6862	14.6938 TO 18.0519
S5	5	18.9700	.3623	.1620	18.5202 TO 19.4198
S8	7	17.6143	1.0245	.3872	16.6668 TO 18.5618
S10	5	17.5940	1.0514	.4702	16.2885 TO 18.8995
Total	24	17.5304	1.4866	.3035	16.9027 TO 18.1582

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= .8806 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 3.95

	NS	S10	S8	S5
NS				
S10				
S8				
S5	*			

(*) Indicates significant differences

Table 44: One-Way Analysis of Variance of Tensile Strength Data Compared between Different Periods of Storage Time, for a composite material

(1) Nonsulfonated PP Composite

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	1.3567	.4522	.2072	.8904
Within Groups	24	52.3925	2.1830		
Total	27	53.7492			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
3-wk	7	16.7643	.9013	.3407	15.9307 TO 17.5979
5-wk	7	16.5000	1.9567	.7396	14.6904 TO 18.3096
7-wk	7	16.1557	.8916	.3370	15.3311 TO 16.9803
9-wk	7	16.3729	1.8155	.6862	14.6938 TO 18.0519
Total	28	16.4482	1.4109	.2666	15.9011 TO 16.9953

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 1.0448 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 3.90

- No two groups are significantly different at the .050 level

(2) 5-min Sulfonated PP Composite

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	1.3585	.4528	.3073	.8198
Within Groups	21	30.9496	1.4738		
Total	24	32.3081			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
3-wk	7	18.5429	1.8146	.6859	16.8646 TO 20.2211
5-wk	6	18.5533	.9585	.3913	17.5475 TO 19.5592
7-wk	7	19.0414	1.0062	.3803	18.1108 TO 19.9720
9-wk	5	18.9700	.3623	.1620	18.5202 TO 19.4198
Total	25	18.7704	1.1602	.2320	18.2915 TO 19.2493

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= .8584 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 3.94

- No two groups are significantly different at the .050 level

(3) 8-min Sulfonated PP Composite

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	2.7873	.9291	.4603	.7128
Within Groups	22	44.4085	2.0186		
Total	25	47.1958			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
3-wk	7	17.9871	1.4640	.5534	16.6331 TO 19.3412
5-wk	7	18.5014	1.7208	.6504	16.9100 TO 20.0929
7-wk	5	17.9860	1.3679	.6117	16.2876 TO 19.6844
9-wk	7	17.6143	1.0245	.3872	16.6668 TO 18.5618
Total	26	18.0250	1.3740	.2695	17.4700 TO 18.5800

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 1.0046 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 3.92

- No two groups are significantly different at the .050 level

(4) 10-min Sulfonated PP Composite

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	4.4226	1.4742	.6157	.6137
Within Groups	18	43.1001	2.3944		
Total	21	47.5227			

Group	Count	Mean	Standard Deviation	Standard Error	95% Confidence Interval for Mean
3-wk	6	18.8550	1.7224	.7032	17.0475 TO 20.6625
5-wk	4	18.1125	1.8469	.9234	15.1737 TO 21.0513
7-wk	7	18.2171	1.5062	.5693	16.8242 TO 19.6101
9-wk	5	17.5940	1.0514	.4702	16.2885 TO 18.8995
Total	22	18.2305	1.5043	.3207	17.5635 TO 18.8974

Multiple Range Tests:
Tukey-HSD test with significance level .050

The difference between two means is significant if
MEAN(J)-MEAN(I) >= 1.0942 * RANGE * SQRT(1/N(I) + 1/N(J))
with the following value(s) for RANGE: 3.99

- No two groups are significantly different at the .050 level

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