AN ABSTRACT OF THE THESIS OF

Bin Xu   for the degree of Master of Science in Chemical Engineering presented on March 15, 1999.   Title: Studies of Polystyrene(PS)/High Density Polyethylene(HDPE) and PS/HDPE/Wood Composites from an Extrusion Process: Mechanical Properties, Rheological Characterization and Morphology

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The global motivation for this work comes from the desire to fabricate "plastic lumber" with improved mechanical properties (particularly creep resistance) from recycled plastics and wood composites. The present studies have utilized "virgin plastics" of polystyrene (PS), an amorphous, stiff material that exhibits brittle fracture, and high density polyethylene (HDPE), a crystalline, tough material, that exhibits yield behavior but no fracture, with wood flour as a filler material. The goal is to achieve materials of high modulus of elasticity (MOE), reasonable strength, and very little creep.

The first phase of the work involved PS/HDPE blends with ratios: 100:0, 75:25, 50:50, 25:75, 0:100. The second phase of the work involved the addition of wood flour (aspect ratio ~ 3.0) at levels of 10 -40wt% to the various plastic blends to make PS/HDPE/WF composites. In both cases, the materials were melt blended in a Banbury mixer and then processed through a single-screw extruder, with a shaping die attachment to make test bars. In some cases, the melt blended samples were compression molded in order to study processing effects. The samples were

characterized using rheological, thermal (DSC), and morphological (SEM) techniques, and the mechanical properties (MOE, strength, creep) were measured.

Differential scanning calorimetry (DSC) indicates that the PS/HDPE blends are phase separated at all compositions, with the major and minor phases changing with composition and processing history. As was determined from SEM measurements, the HDPE remains the continuous phase up to 75% PS and a ribbon-like PS phase is observed in extruded samples. The MOE of the blends can be estimated by a weighted average of the blend components while the strength values generally fall below the weighted average value. Creep resistance is generally increased with increasing PS content. Processing history also has a significant effect on the blend mechanical properties, as evidenced by an elongated PS dispersed phase from an extruded blend which increased the strength by more than 50% and decreased the MOE by 25% as compared to a compression molded sample.

The PS/HDPE/WF composites exhibit changes in MOE, strength, and deformation behavior (rupture to yielding) with blend composition, wood flour content, and processing history. In general, MOE increased with increasing WF and PS content as was expected. The strength increases slightly with WF content for "HDPE-rich" composites, up to about 30wt% WF. Poor mixing affects properties at higher %WF content. Strength decreases with WF content for "PS-rich" blends, with the largest

decreases for pure PS composites. The nature of the fracture also changes from yielding to brittle in these extruded "PS-rich" composites.

SEM images show that HDPE adequately coats the WF in the melt phase, but that there is very little adherence of HDPE to WF in the solid state. However, solvent extracted PS/HDPE/WF composites indicate that the WF does preferentially adsorb to the PS. The strength of the PS/WF cannot be determined. The SEM images also indicate that the aspect ratio of the WF is decreased with processing, which has implications the effectiveness of WF as a filler material. The previous "ribbon-like" structure observed in PS/HDPE extruded blends is not seen in extruded composites of similar composition, which helps to explain the strength change from a yielding to a more brittle nature.

The creep response of the composites has been evaluated with a three-parameter power model, from which "creep speed" can be determined. The creep speed is reduced with increasing PS content, and to a lesser extent, with increasing WF content. Samples of 75%PS-25%HDPE with varying WF content exhibited the lowest creep speed. The result is encouraging, indicating that PS/HDPE/WF composites may indeed lead to improved mechanical properties. Further studies using compatibilizers to increase adherence of the WF to the plastic matrix, higher aspect ration wood filler, and processing which allows for improved mixing (static mixers) are recommended.

Studies of Polystyrene(PS) /High Density Polyethylene(HDPE) and
PS/HDPE/Wood Composites from an Extrusion Process:
Mechanical Properties, Rheological Characterization and Morphology

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CONTRIBUTION OF AUTHORS

Dr. John Simonsen was involved in the design, analysis of the general project. Dr. John Simonsen and Dr. Rochefort also assisted in the data collection, analysis, interpretation, and the writing of the manuscripts.

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Chapter 1

INTRODUCTION

Introduction

"Plastic lumber", an alternative for timber as a building material, which has received considerable public attention recently, is recycled plastics extruded in the shape of dimension lumber. There are several factors which encourage the appearance of this new material. First is the increasing demand for building materials as a result of the population explosion, and the decreasing availability of quality timber. Second is the increasing need for proper technology to encourage recycling of plastics. The lack of a suitable end market for mixed recycled plastics is regarded as the one of the most important factors which hamper plastics recycling [1].

However, compared with solid wood, plastic lumber has poor mechanical properties. The tensile strength and stiffness are typically one fourth or less than

that of solid wood. In addition, the poor creep properties of plastic lumber have caused some in-field replacements in Florida [2]. Therefore, considerable improvement in the mechanical properties of plastic lumber are needed before it can gain acceptance as a building material.

The poor creep response is caused by the low stiffness of the thermoplastics. The mechanical properties can be improved by adding reinforcing filler while retaining processability by normal methods such as injection molding and extrusion. Wood fiber is an attractive source of filler, and has been widely used as reinforcing materials in plastic composites. It is cheaper, lighter, and more economical compared to other traditional reinforcing materials such as glass [3]. Using wood filler encourages wood recycling, and the reuse of wood waste products.

Polystyrene (PS) and High Density Polyethylene (HDPE) are two of the most widely used plastics in the world [4]. Their mixture creates mechanical properties which are stronger than HDPE alone, and not as brittle as PS. Plastic lumber made of recycled PS and HDPE is commercially available, and the morphology and mechanical properties have been studied by Li [5,6]. PS and HDPE are incompatible which means that they exist as separated distinct phases in the blends. The morphology observed in the large dimension plastic lumber is created by the competition between the relaxation time of each polymer in its separated phase and process time[7]. Previous studies of PS/HDPE blends have concentrated on compatibilization of the polymers and the resulting effect on the

morphology [8-11], and mechanical properties [12-16]. A variety of compatibilizers have been used with varying success. It is generally accepted that smaller dispersion size results in better mechanical properties [17]. An interlocking structure has been observed in compatibilized PS/Polyethylene(PE) blends by Yang [8]. The effect of morphology on the impact strength of the blends was observed by Barentsen[13] in a PS/Low Density Polyethylene (LDPE) blend.

Studies of wood filled PS/HDPE blends have reported that the addition of fiber increases the stiffness[18]. A differential scanning calorimetry (DSC) study indicated no interaction between the HDPE phase and other phases present in the composite. However, DSC and Scanning Electron Microscope (SEM) results suggest a possible interaction between the PS phase and the wood filler.

Creep is a complex phenomenon and a persistent problem with plastic lumber. The applied stress, the ambient temperature, and the humidity are the primary external factors that effect the creep response of a thermoplastic. The processing effects arise from the molecular state of the test sample which may include molecular orientation, and crystallinity (if any)[19]. The inclusion of wood fibers introduces several additional parameters which effect the mechanical and creep behavior of the reinforced thermoplastics. These parameters include the fiber volume fraction, the fiber aspect ratio, and the orientation of fibers which arise during processing.

In the studies reported in this thesis, the mechanical properties (strength and stiffness) and the creep response of various plastic blends (PS/HDPE) and plastic/wood fiber(WF) composites (PS/HDPE/WF) will be reported. Several analytical techniques have been used to relate the morphological (SEM), thermal (DSC), and rheological properties of the blends or composites to their performance characteristics. The thesis is divided into two sections: PS/HDPE blends, and PS/HDPE/WF composites. It must be emphasized that all of the studies reported in this thesis, "virgin" and not "recycled" plastics have been used. This has been chosen for both convenience (difficult to get consistent recycled plastics) and clarity of interpretation of results.

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Chapter 2

LITERATURE REVIEW

There is a relatively small body of literature which relates directly to the Polystyrene/High Density Polyethylene/wood fiber composites. However, PS/PE blends, PS/WF and PE/WF composites have been studied considerably. The polyethylene (PE) in these studies may be High Density Polyethylene(HDPE), Low Density Polyethylene(LDPE), or Linear Low-Density Polyethylene (LLDPE). The mechanical properties of PS/PE/WF composite must strongly depend on the morphology and the interaction between any two of these materials, as well as individual materials. The literature review will examine all aspects of this composite - the PS/PE blends, PS/WF, HDPE/WF and PS/HDPE/WF composites.

Polystyrene/Polyethylene Blends

PS/PE blends can be compression molded[1-4], extruded[5,6], or made from a rolling mill[7,8]. PS/PE blends are always incompatible (i.e., phase separated). Depending on composition and processing, either the PS or PE can be considered the dispersed phase. In the case of PS as the dispersed phase, either

elongated (ribbon or rod-type) or droplet-type PS were observed[9]. Elongated structures which change to the lower surface energy droplet state upon annealing have also been observed[5]. When the PS content increased, the PS domains also increased, and were largest in the 50% PS composition. The continuous phase inversion may happen around 50% PS content[8]. In the case of PE as the dispersed phase, PE could also be in a droplet[1,3], or fiber shape[10]. The development of either the droplet or fiber-like microstructures in the minor phase of an extrusion process is believed to be a function of the viscosity ratio of polymers (relaxation times) and the processing shear stress and time.

The effect of molecular weight on the blend morphology has also been investigated with PS as dispersed phase[8]. For low molecular weight PS (M_w=53,000), relatively homogeneous blends of spherical, separated PS domains of two distinctive sizes were observed (0.2-0.4 and 1-5 μm). As the molecular weight of PS was increased, the small domains disappeared, while the other domains clearly enlarge. When high molecular weight PS was studied (M_w= 230,000), highly nonhomogeneous structures are formed (mainly ca 10 μm PS domains).

The morphological development (vs. Processing time) during the blending of LLDPE and PS has been studied in detail by Yang and his collaborators with a Haake Internal Mixer[7,11]. The resulting mixture shows a bimodal particle size distribution of the minor phase at the initial mixing stage where the most significant changes in phase morphology occur. The reduction mechanism for droplet size is

primarily effective in reducing the number of the largest droplets rather than decreasing the diameters of all the droplets. When a compatibilizer is used, the rate of the droplet breakup is increased and the smaller particle size of the minor phase is achieved earlier in the blending process, due to the reduction of the interfacial tension between the PS and LLDPE phases.

The PS and PE may both appear as continuous phase, and was regarded as co-continuous phases. The co-continuous phase phenomena have been observed by different authors in PS/LLDPE[1], and PS/LDPE[3,12] systems. The co-continuous phases resulted in an intermediate Modulus of Elasticity (MOE)[12] between pure PS and PE. For PS/LDPE blends, which contained small amounts of LDPE (20%), the co-continuous phase morphology was observed, but is very unstable in the absence of emulsifier or compatibilizer[3].

PS and PE are incompatible with each other[9]. This causes weak adhesion between the PS and PE phases and poor strain transfer inside the blend which, eventually, leads to poor mechanical properties for the PS/PE blends. The studies were therefore focused on the compatibilization, and the effect of a compatilizer on the morphology[1,11,13], and the mechanical properties[1,12,14-16]. It is commonly believed that the smaller dispersion size related to better mechanical properties.

Almost all compatibilizers were block copolymers which possess at least two blocks similar in structure or chemistry to PS and PE respectively, and could "tie" two phases in the blends. Polystyrene-*block*-polybutadiene(SEB) and

polystyrene-*block*-polybutadiene-*block*-polystyrene(SEBS) were used to study the PS/LDPE blend[1]. These saturated block copolymers were effective in reducing the PS, the dispersed phase, domain size.

Yang and his co-workers[7,11] studied the compatibilization effects of Styrene-ethylene/propylene(SEP) diblock and SEBS triblocks on the PS/LLDPE blends. The addition of SEP and SEBS not only reduces the dispersed-phase size but also results in an interlocking structure. The tendency toward forming the interlocked structure is determined by the interdispersion and the molecular structure of the copolymers. The efficiency of compatibilizer varied because of the difference of the compatibilizer molecular weight and chemical structure. SEBS was reported to behave much more efficiently than SEP in compatibilizing PS and LLDPE[11].

Besides improving the compatibility, another approach to improve the mechanical properties of incompatible polymers is to take advantage of polymer processing. PS/PE blends, produced by the combination of extrusion and mechanical stretching of the melt prior to quenching, possess considerably higher tensile strengths and ultimate elongation in machine direction than those obtained from compression molded blend's samples[17]. The highly stretched blends have a fibular morphology in which the two components are parallel to one another, and showed superior mechanical properties in machine direction. While the transverse tape properties were poor due to poor interfacial adhesion.

PE/Wood-fiber Composites

For PE/Wood Fiber composite, the studies have focused on the fiber dispersion, fiber length, fiber orientation and interfacial adhesion between wood fiber and the polymer matrix.

Benzoyl peroxide, dicumyl peroxide, ploy(methylene)-ploy(phenyl)isocyanate (PMPPIC), silane were used as surface modifiers for the wood fibers to improve the interfacial bonding. The rheological behavior with or without these additives has been reported by George[18]. Melt viscosity was found to be increased with fiber loading. Treatments based on PMPPIC, silane and peroxide increased the viscosity of the system due to high fiber-matrix interfacial interaction. The urethane derivative of cardanol was used by Joseph to treat the sisal fiber[19]. The treated sisal fibers/PE composites possess higher tensile strength than untreated and glass-fiber filled composites.

Besides the chemical additives, Corona treatment has also been used to modify PE/Cellulose composites[20]. The results show clearly that corona treatment is effective in increasing the ductility of composites and in increasing the yield strength. The effects of corona are particularly noticeable in composites where both constituents are corona-treated or where the cellulose fiber is so modified.

Folkes[21] demonstrated that for short wood fiber reinforced plastic composites, only the fibers which are longer than the critical length can contribute to the improvement of mechanical properties. The critical fiber length is a function

of the critical shear stress between the fibers and the matrix[22]. The improvement of interfacial bonding will result in a shorter critical length, which, eventually, led to better mechanical properties for the same fiber length distribution. Dong[20] reported that the wood fiber length in an untreated PE matrix must be greater than 0.83mm to ensure an effective transfer of stress. However, the corona treatment of PE reduces the critical length for stress transfer to 0.27mm.

The composite processing will effect the fiber length, which may eventually deteriorate the mechanical properties. Reductions in composite strength and Young's moduli occur due to fiber breakage at higher rotor speeds[23]. To avoid this situation, the fibers were added after the polymer is melted.

For large aspect ratio fibers, the fiber orientation is an important issue. The composites in which the fibers are orientated in a longitudinal direction have a much higher tensile strength, Young's Modulus, and tear strength than those composites with random fiber orientation[23].

Fiber loading effects have also been extensively investigated. Basically, the strength and modulus increase with the wood fiber content up to some fiber loading point. For short pineapple-leaf-fiber-reinforced LDPE composites, it was observed that by adding 10% fiber there is an increase of 90% in tensile strength, and 300% in Young's modulus. Above 10% fiber loading, the increase in tensile strength and modulus is less pronounced [23]. This is possibly due to increased fiber-to-fiber interactions at the higher loading. A similar phenomenon has also been observed in sisal fiber-reinforced polyethylene composites[23]. Tensile strength and modulus

increase with fiber content up to 20% in weight, and then decrease at 30% fiber loading.

Wood fibers do not easily disperse in non-polar polymers such as PE. It was reported, for HDPE/wood fiber composites, that the tensile strength decreases monotonically with increasing fiber content, and was attributed to the poor fiber dispersion during composite fabrication[24]. Stearic acid [22] and carboxylic waxes[15] were used to improve the dispersion.

The reinforcement of two or more type of fibers into a single matrix leads to the development of hybrid composites with a great diversity of material properties. The hybrid composite properties of Sisal/LDPE/Glass fiber composites have been studied by Kalaprasad[25].

The theoretical modeling of tensile properties of short sisal fiber-reinforced LDPE has been presented by Kalaprasad [26].

PS/Wood-fiber Composites

Unlike the PS, which is a non-polar hydrophobic material, wood fiber is a polar material because of hydroxyl groups which exist in its constituent polymers. This generally results in poor compatibility between PS and wood fiber. For this reason, a lot of work has been directed towards the use of compatibilizers to enhance the PS/Wood fiber adhesion.

Liang[27] tried to use polystyrene/poly(methacrylic) (both low and high molecular weight) and polystyrene/poly(vinyl acetate) as coupling agents to promote compatibility in a PS/wood fiber system. The tensile strength decreases with increasing filler content in composites without additives. After the coupling agents were added, the tensile strengths increases with increasing filler content, but were still smaller than that of pure PS. It was found that the type of coupling agent is the factor primarily responsible for retaining the tensile strength. Among the coupling agents Liang used for the system, polystyrene/poly(methacrylic) acid was the most effective with regard to enhanced tensile elastic modulus at higher fiber-loading levels (enhancement levels of 11.3-23.8% over pure PS).

Sawdust[28,29] (20 and 60 mesh size) were used by Maldas as reinforcing fillers in a PS system. The effect of wood species on the composite mechanical properties have been studied. Spruce sawdust is slightly better than that of aspen sawdust [28,29]. It is also found that the smaller particles improve the mechanical properties more than larger ones. Poly[methylene(polyphony isocyanate) (PMPPIC) acts as a good reinforcing agent and improves the interfacial contact between fiber and polymer [28-30]. The role of PMPPIC as a coupling agent can be explained in the following way. The functional group -N=C=O in isocyanate reacts chemically with the -OH group of cellulose as well as lignin to form urethane bonds. As a result, the isocyanate parts are linked to the cellulose matrix by a chain of covalent chemical bonds. The delocalized π-electrons of the benzene rings of

both PS and PMPPIC provide a strong interaction, which help to promote adhesion at the PS/wood fiber interface. The increased interaction leads to improved mechanical properties.

Except the PMPPIC and isocyanate, silane and polystyrene grafting to wood fibers were also studied to improve the compatibility[30]. Generally, the improvement, if any, is about 10%[30].

A more detail studies of polystyrene and wood fiber has been carried by Furuno[31]. The location of polystyrene in the fiber cell wall was determined. It was found that the wall polymer played an important role for the dimensional stability of fiber. This conclusion is in agreement with the conclusion that wood filler can act as a reinforcing agent[28].

Generally, the compatibility improvement in PS/wood fiber composite system has been widely studied, and achieved greater success compared with the PE/wood fiber system.

PS/HDPE/Wood-fiber Composites

Polyethylene was used as a coating polymer for PS/wood fiber composites[32] by D. Maldas. The strength of coated composites are inferior to the untreated, while modulus could be improved in certain wood filler range. Among the PE (LLDPE,MDPE,HDPE) used in the research, the performance of LLDPE and HDPE is better.

The addition of PS to high density polyethylene (PE) significantly improved strength and stiffness[33], with a 35% PS content showing the best results. The material properties of composites produced from recycled PS, HDPE and recycled wood fiber were compared by Simonsen[34]. Stiffness was generally improved by the addition of fiber, as expected, but brittleness also increased. Pre-treatment of the wood filler with phenol-formaldehyde resins did not significantly effect material properties.

There was very little literature for PS/HDPE/Wood fiber composites. As a preliminary study of this composite system, PS, HDPE and wood flour were used without compatibilization. The emphasis was focused on the feasibility to improve the creep response.

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Chapter 3

MECHANICAL PROPERTIES AND CREEP RESISTANCE IN POLYSTYRENE/HIGH DENSITY POLYETHYLENE BLENDS

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Abstract

Recycled plastics, predominately high-density polyethylene (HDPE), are being re-extruded in the shape of dimension lumber and marketed as "plastic lumber." One drawback to these products is their low creep resistance, or high creep speed. The objective of this study was to examine the feasibility of reducing the creep speed of PE-based products by blending the PE with a lower-creep plastic, in this case polystyrene (PS). Various blends of HDPE and PS were prepared in either a laboratory extruder or a bowl mixer and then compression-molded. The mechanical properties, creep resistance, morphology, and thermal properties of extruded and compression-molded samples were determined. The modulus of elasticity of the extruded blends could be estimated by a weighted average of PS and HDPE even in the absence of a compatibilizer. Processing strongly affected the mechanical properties and morphology of the blends. For 50% PS:50% HDPE blends, the stress-strain curves of the extruded samples showed PE-like behavior, whereas those from compression-molded samples were brittle, PS-like curves. Flexural strength was 50% higher in the extruded samples than in those from compression molding. The creep experiments were performed in three-point bending. Creep speed was lower in 50% PS:50% HDPE and 75% PS:25% HDPE blends than in pure PS. Creep speed of 75% PS:25% HDPE was lowest of all the extruded blends. HDPE formed the continuous phase even when the PS content was as high as 50% (wt). For a 75% PS:25% HDPE blend, co-

continuous phases were observed in the machine direction. A ribbon-like PS dispersed phase was observed in the 25% PS:75% HDPE and 50% PS:50% HDPE samples. Blending low-creep-speed PS with high-creep-speed HDPE appeared to improve the performance of the final composite successfully.

Introduction

Polystyrene (PS) and high density polyethylene (HDPE) are two of the most widely used plastics in the world[1], with annual production rates in the hundreds of billions of pounds. Less than 10% of this production is currently recycled, for a variety of reasons[2]. One use for recycled plastics, especially HDPE, is extrusion into shapes resembling lumber—thus the term "plastic lumber." These products are used as building materials in a variety of applications, including decking, landscaping, signs, and outdoor furniture. One drawback to some plastic lumber products is their tendency to creep. This is especially true for those products composed primarily of HDPE.

Creep in plastic lumber products may be reduced by blending the low-creep-resistance (or high-creep-speed) HDPE with a lower creep-speed plastic, such as PS. These blends may also possess mechanical properties intermediate between PS and HDPE; they therefore may be tough, but not as brittle as PS alone. They also may possess good elongation, but be less ductile than pure HDPE. This kind of blend might also provide a useful matrix for wood/plastic composites[3]. The objective of this study was to investigate the feasibility of improving the performance of HDPE as a material for the manufacture of building materials by blending it with PS.

PS is incompatible with polyethylene(PE)[2]. Blends of these compounds consist of mixtures of phases of the two components, either dispersed or

continuous. Typically these blends exhibit weak adhesion—i.e., poor stress transfer—between the PS and PE phases, which manifests as inferior mechanical properties in the final composite. Most previous studies have focused on compatibilization of the phases. Almost all compatibilizers reported have been block copolymers consisting of at least two blocks, with one block similar in structure or chemistry to PS and another similar to PE. Thus, the diblock copolymer "ties" the two phases together. The effect of compatibilization on the morphology of the blend[4-7] and its mechanical properties[8-12] has been well studied. Compatibilization promotes the formation of an interlocking structure in PS/PE blends, which allows more equal sharing of imposed stresses and might therefore improve the mechanical properties of the blends[8].

PS/PE blends can be made in several ways: by compression molding[10,13] by coextrusion[14,15] or with a rolling mill[4,5,16]. Generally, the morphology of the resulting blend is related to its processing history. The morphology of the blend is strongly related to its mechanical properties. Usually, smaller sizes in the dispersed phase produce better mechanical properties[12]. The size and shape of the minor phase are critical to the impact properties[17,18]

Compared with other engineering materials, plastics possess low creep resistance. For a perfectly elastic solid, the creep compliance (J) is inversely proportional to tensile modulus[19]. Thus, the modulus gives some indication of the tendency to creep. Nielsen[20] has shown that the ratio of creep compliance of

the filled or unfilled polymers is inversely proportional to the ratio of the tensile

modulus of the filled and unfilled polymer.

$$\frac{J}{J_0} \equiv \frac{E_0}{E} \qquad\qquad (3\text{-}1)$$

where J_0 is the creep compliance for the unfilled polymer and E_0 and E are the

tensile moduli of elasticity for the unfilled and filled polymers, respectively.

Creep resistances intermediate between those of neat PS and HDPE were

expected for PS/HDPE blends, but not found. There are no literature reports on

creep resistance in this blend system.

In this study, the mechanical properties, morphology, and creep behavior of

PS/HDPE blends from an extrusion process were investigated. The results were

compared with those from blends formed by compression molding.

Experimental

Materials

HDPE was contributed by Phillips Petrochemical Company (Houston, Texas) as Marlex EHM 6007. The molecular weight was 120,000 (by gel permeation chromatography); the density, 0.964 g/cm^3; and the melt index, 0.65 g/10 min (190°C/2 kg). PS (Dow 685D) was contributed by Dow Chemical Corporation (Midland, MI). The weight-average molecular weight was approximately 300,000; the density, 1.04 g/cm^3; and the melt index, 1.5 g/10 min (200°C/5 kg).

Processing

The plastics were received as pellets and were dry-mixed before going through a 19mm (3/4-in.) single-screw Brabender extruder attached to a Brabender Plastic drive unit. The Brabender extruder was operated at 40 rpm, with the barrel temperature set at 170°C for all heating zones. The temperature at the die region was measured as 180°C. A rectangular die (2 × 12 mm) was attached to the extruder. The pressures were in the range of 1–2.5 MPa, depending on the material extruded. A typical extrusion rate was 1.2 m/min. To compensate for the die swell, a shaping die was placed 5–8 cm downstream of the extrusion die. Water was used

to cool and solidify the extrudate at the shaping die. A puller was placed downstream from the shaping die and manually synchronized with the extruder to minimize drop in the extrudate as it exited the rectangular die. Test bars (60 mm) were cut from the cooled extrudate and chosen randomly for testing.

Samples were also prepared in a Brabender Plastic bowl mixer with cam blades attached. The mixer speed was set at 30 rpm and 177°C. Typical mixing time was 10 min.

The samples from the bowl mixer were ground in a Wiley mill to a particle size of approximately 3 mm (0.1 in.) before compression molding. The blends were then compression-molded in a thermostated Carver laboratory press. The press conditions were 180°C and 6.9 MP for 10 min. The samples were then cooled to room temperature under pressure at ambient temperature. The molded samples were $2 \times 13 \times 55$ mm.

Testing of Mechanical Properties

Mechanical properties were determined with a 3-point bending apparatus in accordance with ASTM standard D 790-86. Whenever possible, five samples were tested for each determination of the modulus of elasticity (MOE), and the ultimate stress. The crosshead speed was 1.3 mm/min. The samples were flattened by

filing. Typically it was difficult to obtain a flat molded sample with a high HDPE content.

Ultimate stress is defined in different ways, depending upon the fracture behavior of the material:

1. Modulus of rupture (MOR): In this case, the stress increases with strain until samples break cleanly. This is brittle fracture, which was observed only for the compression-molded 100% PS samples.

2. Yield strength (YS): The yield strength is defined as the first point at which the stress-strain curve shows a slope of zero. This point is reported for those samples (the 25, 50, and 75% PS blends and the extruded 100% PS) that either yielded before breaking or did not break but continued to bend to the limits of travel of the testing machine.

3. Offset yield strength (OYS): In the cases where the samples neither broke nor showed a yield point (100% HDPE), the stress-strain curve did not show a slope of zero, but rather rose smoothly to the limits of travel of the testing machine. In these cases, the ultimate strength was reported as the 0.5% strain offset yield strength. This was calculated with the method specified in ASTM standard D790-86 and described in ASTM standard D638-89.

The creep experiment was done in an environmental chamber set at a 19.5°C and 50% relative humidity. The specimens were 1.71 ± 0.01 mm (mean ± S.D.)

thick. The span/thickness ratio (L/D) was 20.0 ± 0.2. The creep tests were performed at a load of 50% of the ultimate strength unless otherwise indicated.

Density

The density of samples was measured by a buoyancy method with a Denver Instrument XE-310 balance (1mg resolution). The samples were submerged in water with fine copper wire. The density of the water was assumed to be 1.00 g/cm^3, so the weight of the displaced water was equal to the volume of the submerged sample and wire. The density was calculated as

$$d = \frac{W}{V_{total} - V_{cu}} \qquad (3\text{-}2)$$

where d = density (g/cm^3), W = sample weight (g), V_{total} = weight of displaced water for submerged sample and wire (g), and V_{cu} = weight of dispersed water for submerged wire (g).

The standard deviation of the measurements was 0.002 g/cm^3.

Microscopy

Phase morphology was examined with an AmRay 1000A scanning electron microscope (SEM). The samples were dipped in liquid nitrogen and then fractured. In order to increase the contrast and observe the matrix and the dispersed phases, selected samples were soaked in toluene at room temperature to dissolve the PS phase of the blend. All samples were coated with a Au-Pd film (8–10 μm) before imaging. The SEM was operated at 10 kV on Polaroid type 55 positive-negative film.

Rheological Testing

The relaxation times of polymers and blends were measured with a Bohlin CS-50 rheometer. The samples were molded to discs of 25mm diameter and 1mm thickness. The molding temperatures were 160°C for HDPE, 175°C for 50% PS:50% HDPE and 195°C for PS. The samples were held at the molding temperature for 30 min. Dynamic Oscillatory shear tests were performed for these samples to obtain elastic moduli (G') and viscous modulus (G'') at various oscillation frequencies (ω). The relaxation time (τ) was calculated as[21]

$$\tau = \frac{1}{\omega_c} \qquad\qquad (3\text{-}3)$$

where ω_c is the crossover frequency where $G' = G''$

Differential Scanning Calorimetry (DSC)

The thermal behavior of the samples was characterized using a Shimadzu differential scanning calorimeter with a TA50 software package. The temperature was ramped at 10°C/min in a range of at least 70°–160°C. If a second run was performed, the samples were slow cooled in ambient conditions and then taken as in the first running.

Results and Discussion

Mechanical Properties

MOE

The MOE of the blends varied as the weighted average of the HDPE and PS components [Fig. 3.1A], as expected. Since the MOE is measured in the elastic phase of the blend, polymer incompatibility should have little effect on the composite MOE. The compression-molded samples had a higher MOE than did the extruded samples, with the MOE of compression-molded 50% PS:50% HDPE (2.26 ± 0.05 GPa) about 25% higher than that of extruded samples (1.87 ± 0.11 GPa). (Results are expressed as mean ± S.D.) A similar increase in ductility in extruded PS was also observed by Stell[22], but without interpretation.

Strength

The flexural strength of PS/HDPE blends increased with increasing PS content, but was lower than that predicted by a simple weighted average of the components [Fig. 3.1B] (which would be a straight line connecting 100% HDPE
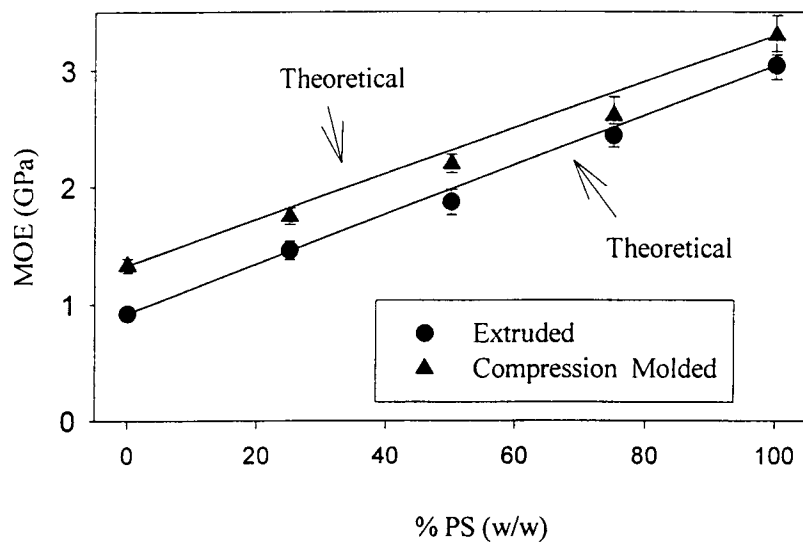
Figure 3.1A   Modulus of Elasticity (MOE) for Extruded and
Compression-molded PS/HDPE Blends
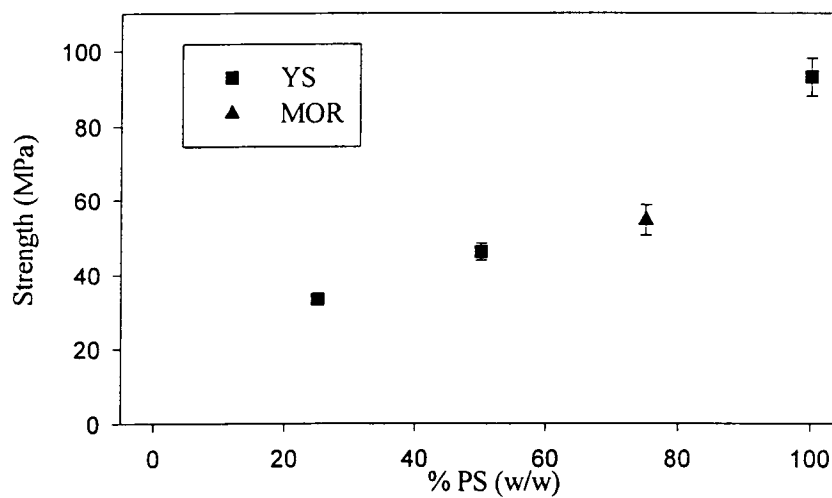
Figure 3.1B Flexural Strength of Extruded PS/HDPE Blends

and 100% PS). This is typical of blended systems with poor interfacial adhesion[10,23]. Interpretation of the data was complicated by the varying fracture modes of the samples. Extruded PS is yielding and HDPE is ductile. As the PS content increased, the appropriate strength measure changed from offset yield strength (OYS) (0.5% strain was chosen) for 100% HDPE, to yield strength (YS) for 25%, 50% and 100% PS.

Because the 75% extruded samples showed brittle fracture, the strength was reported as the MOR. Li[17] reported a similar result. Processing greatly influenced the strength of the blends. At 50% PS:50% HDPE, the extruded sample was about 50% stronger (46.1 ± 0.5 MPa) than the compression-molded sample (29.8 ± 1.5 MPa).

The difference in mechanical properties caused by processing was hypothesized to be due to an elongation of the polymer by force exerted on the extrudate by the puller and the rapid cooling of the extrudate at the shaper die. The birefringence of 100% PS under polarized light gave further evidence of elongation and indicated some degree of alignment in the PS phase. Annealing an extruded PS sample at 125°C for 24 h removed the birefringence in the PS and shrank the sample length by 65 to 75%. Thus, the processing appeared to introduce some degree of elongation, or pultrusion, into the extrudate.

Creep

All the samples showed some creep [Fig. 3.2A]. A linear transition of decreasing creep with increasing PS content was not observed. The 50% PS:50% HDPE and 75% PS:25% HDPE blends showed lower creep than 100% PS, with 75% PS:25% HDPE exhibiting the least creep of all the samples tested.

Unexpectedly, compared with compression molded PS, extruded PS did not break clearly, but yielded, and showed lower stiffness. These process effected material properties may have resulted in the lower creep resistance for 100%PS observed in Fig.3.2A. For 75%PS:25%HDPE, and 50%PS:50%HDPE blends, HDPE was the continuous or co-continuous phase, and the processing conditions were also slightly different, therefore, the stress transferred to dispersed or co-continuous (in the case of 75%PS:25%HDPE) PS phase may have been different from that of the pure PS. This may have resulted in the different creep response observed for these two blends.

The different samples also showed different initial deflections. This is because they were loaded at 50% of estimated ultimate stress, which was a different load for each sample type. Since the stiffness also varied, but not linearly with the strengths, the initial deflections were different for different sample types.

Creep was further characterized with a mathematical model, expressed as the empirical power function equation[24]

$$\varepsilon = \varepsilon_0 + at^b \qquad\qquad (3\text{-}4)$$

where ε is the specimen deformation at time t, ε_0 is the initial deformation, and a and b are fitting parameters. This equation was used to fit the deformation versus time data and gave R^2 values > 0.85 (Table 3.1). The creep speed was defined by taking the time derivative of equation (3-4):

$$V_c = ab\, t^{b-1} \qquad\qquad (3\text{-}5)$$

where V_c is the creep speed.

V_c is a complicated, nonlinear function of the PS content [Fig. 3.2B]. At 1 h, the creep speed decreases rapidly with increasing PS content up to 75% PS. Within experimental error, 100% PS exhibited the same creep speed as the 75% PS:25% HDPE sample. However, the creep speed is also a function of time. At t = 500 h, the creep speed was remarkably less in the 50% and 75% PS content blends than in the other samples. The 100% PS sample showed a creep speed similar to 100% HDPE at 500 h.

In Fig. 3.2A, the 100% PS sample is showing accelerating creep speed, usually a prelude to fracture, while the 50 and 75% PS blends appear stable, with low creep speeds. This anomalous behavior may perhaps be explained by the processing conditions. The blends were all extruded at the same temperature and at similar pressures, with PE appearing to be the continuous phase in the PS/HDPE blends. Thus, the viscosity of the continuous phase in the blends would be lower

than that of the 100% PS sample. These differing viscosity may have given rise to differing amounts of elongation of the PS. The number of variables that control the elongation is large: melt viscosity, flow profile of the melt through the die, rate of cooling, and others. Thus, we cannot predict the elongation for these different systems, yet they may affect the elongation, and thus the moduli and creep response, of the samples.

The extruded samples of 50% PS:50% HDPE showed a larger initial creep speed (V_c) than did compression-molded samples. This is because their actual load was greater, as a result of their greater strength, but their MOE values were smaller than those for compression-molded samples. Thus, we would expect a greater initial deformation. However, they showed similar V_c values: 0.08 ± 0.02 for the extruded samples and 0.07 ± 0.04 for the compression-molded samples. The different morphologies did not result in different creep speeds within our experimental error.
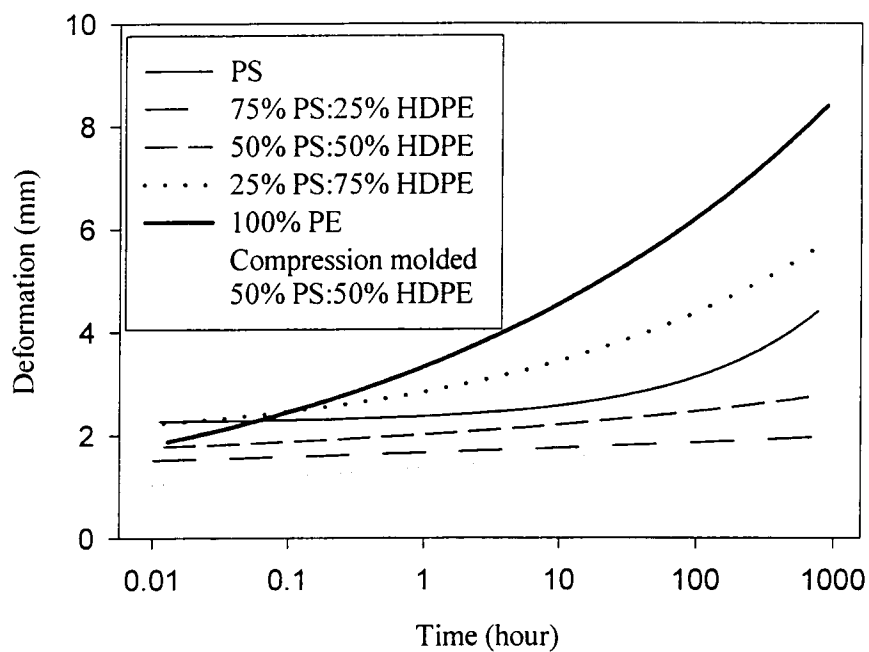
Figure 3.2A Creep Response of PS/HDPE Blends from Extrusion Process
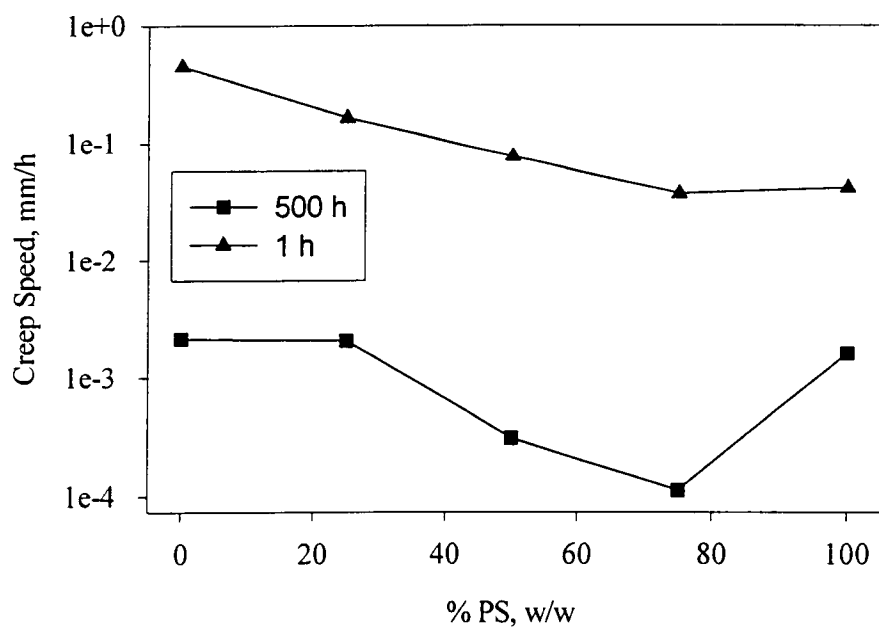
Figure 3.2B Creep Speed (Vc) of PS/HDPE Blends

Table 3.1 Parameters of the Equation Modeling Creep Data
in PS/HDPE Blends [Eq. 3-4]
Values are expressed as means (standard error)

Sample	R^2	ε_0	a	b
100% PS	0.99	2.25 (0.02)	0.12 (.001)	0.44 (0.01)
75% PS:25% HDPE	0.87	1.12 (0.258)	0.54 (0.26)	0.07 (0.03)
50% PS:50% HDPE	0.95	1.47 (0.131)	0.55 (0.13)	0.13 (0.02)
25% PS:75% HDPE	0.94	1.79 (0.27)	1.05 (0.25)	0.20 (0.03)
100% HDPE	0.98	0.13 (0.41)	3.20 (0.40)	0.14 (0.01)

Density

In order to investigate the differences between extruded and compression-molded samples further, the density of the samples was measured. The density for the 50% PS:50% HDPE blend from compression molding (0.970 g/cm^3) was higher than that from extrusion (0.957 g/cm^3). Since DSC measurements showed that the crystallinity of the 50% PS:50% HDPE blends from different processes was almost equivalent (about 51%), these data suggest that there are voids inside the extruded blends. Lahrouni[25] also has attributed the difference between the measured and the calculated density to the presence of voids in PS/PE blends. Shrinkage during PE crystallization is about 10%[18], Thus, the difference in MOE may be due to a

difference in density that arises from a difference in the morphology of the phases in the blended samples. This morphological difference probably arises in turn from processing methods.

Morphology

HDPE was the continuous phase in 100% HDPE, 25% PS:75% HDPE, and 50% PS:50% HDPE [Fig. 3.3A and Fig. 3.3B]. The dispersed PS was elongated in the machine direction [Fig. 3.3A] and was uniformly distributed except at the surface skin region, where HDPE predominated, possibly because of its low viscosity. This "boundary layer" (not shown) appeared to be only about 100 μm thick. The morphology of the 25% PS:75% HDPE blend (images not shown) was similar to that of the 50% PS:50% HDPE.

In other work relating the morphology of elongated, dispersed PS to the shear stress[14], elongated (ribbon-type) PS was observed at the outer part of the samples, and relatively round (droplet-type) PS was found in the interior. This morphology gradient was attributed to competition between the relaxation rate of melt-flow morphology and the cooling rate in the mold. In this study, however, PS was elongated even at the sample center, where no shear stress exists. This suggests that shear stress was not the only factor causing elongation.
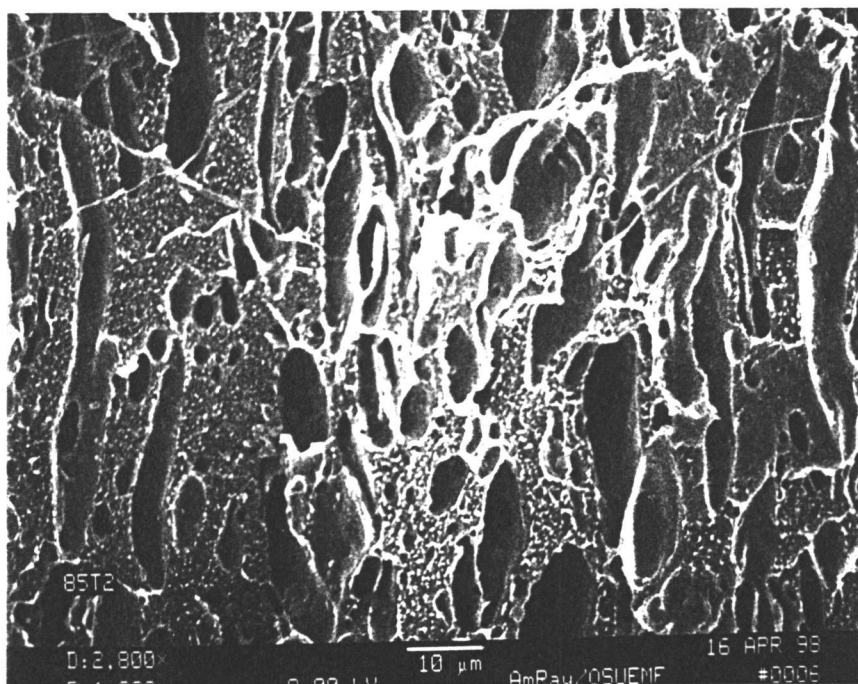
Figure 3.3A SEM of 50%PS:50%HDPE Blend, Machine Direction
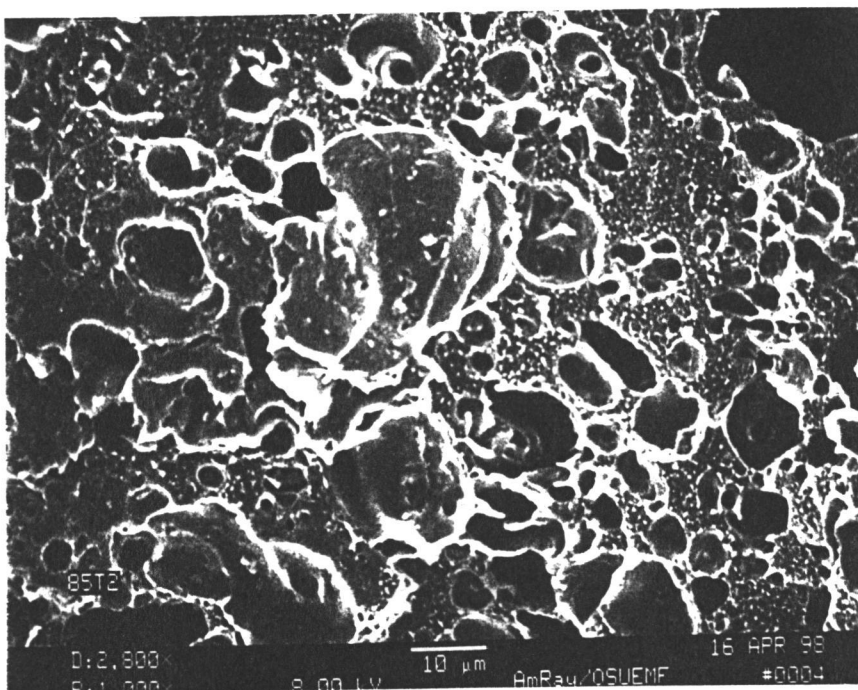
Figure 3.3B SEM of 50%PS:50%HDPE Blend, Transverse Direction
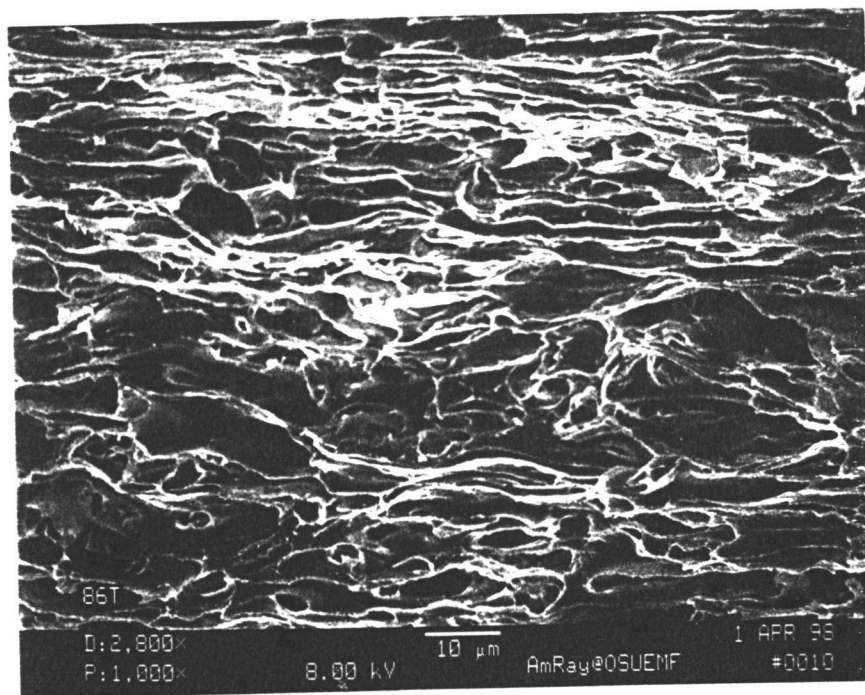
Figure 3.4A SEM of 75%PS:25%HDPE Blend, Machine Direction
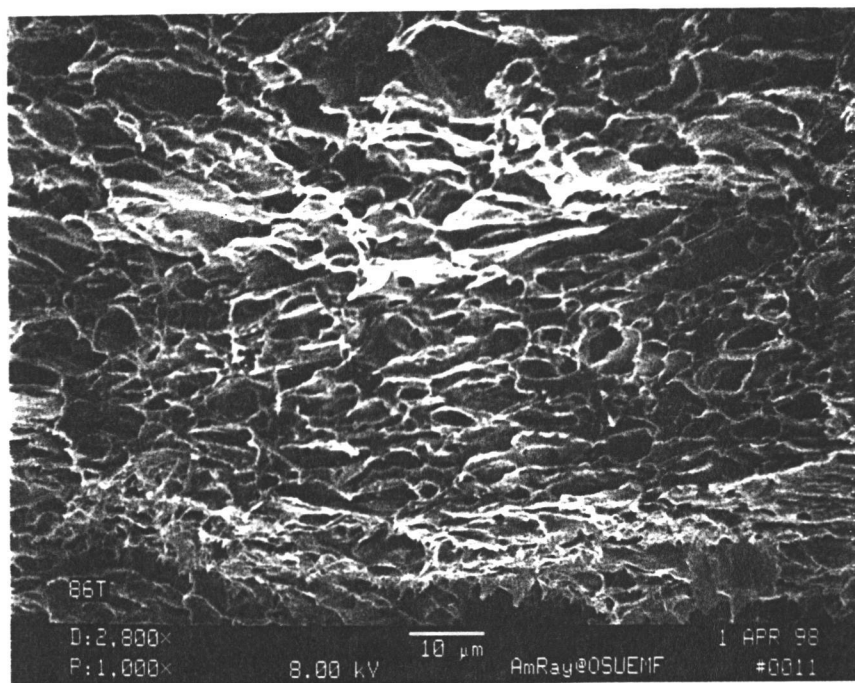
Figure 3.4B SEM of 75%PS:25%HDPE blend, Transverse direction
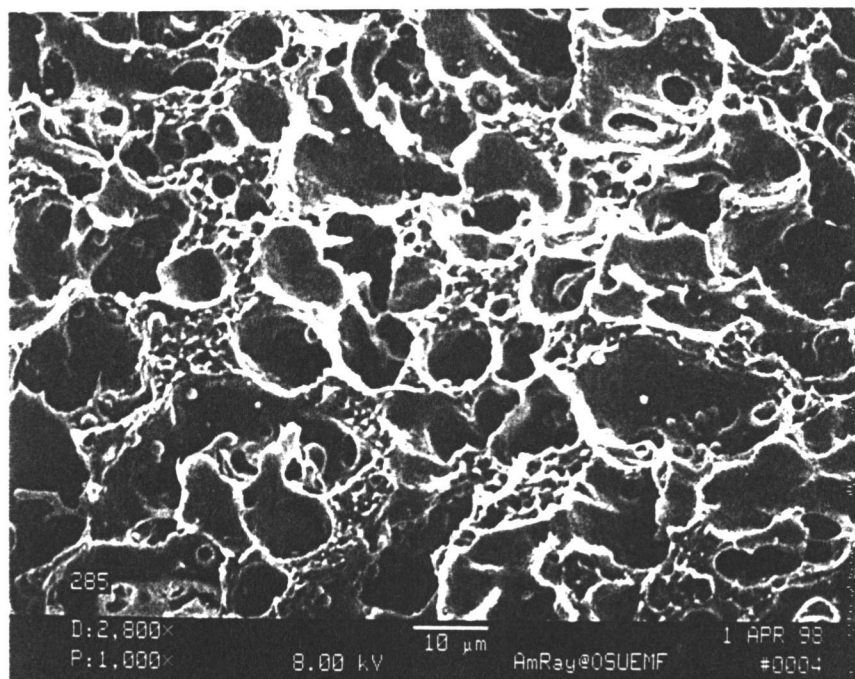
Figure 3.5 SEM of Compression-molded 50%PS:50%HDPE Blend

Since the die was about 1.5 cm long, and the typical extrusion velocity was about 2 cm/sec, the polymers had about 0.8 s to relax. However, rheological testing at 180°C showed that the relaxation time for pure HDPE, 50% PS:50% HDPE, and PS were 0.7, 1.0 and 2.5 s respectively. This suggests that the steady state flow conditions for the PS phase of the plastic blend were not fully developed at the outlet of the die. This factor may have contributed to the pervasive ribbon-like PS distribution.

Pull force was also important in determining the morphology of the blends. The puller was operated so as to maintain a constant tension on the extrudate, which elongated the extrudate and thus gave an elongated, dispersed PS phase. The

dispersed PS was distributed in both droplet and ribbon shapes. The ribbon-type domain was usually about 5–10 μm in width and varied in length. The droplet-type domain was much smaller and was mixed with the ribbon-type PS (Fig. 3.3A).

The 75% PS:25% HDPE blend also showed elongated phases in the machine direction [Fig. 3.4A]. The cross-sectional view showed significant intertwining of PS and PE [Fig. 3.4B].

The ribbon-type morphology was absent from the 50% PS:50% HDPE compression-molded samples (Fig. 3.5). The different processes gave samples that differed in mechanical properties. The yield strength of the extruded 50% PS:50% HDPE (46.1 ± 0.5 MPa) was higher than that of the compression-molded 50% PS:50% HDPE blend (29.8 ± 1.5 MPa). However, the stiffness was reduced in the extruded sample, with an MOE of 1.87 ± 0.11 GPa for extrusion and 2.26 ± 0.05 GPa for the compression-molded sample. The poorer mechanical interlocking in the compression-molded samples relative to that in the extruded samples supports the contention that mechanical interlocking is at least partially responsible for the higher strength observed in the extruded samples. The co-continuous phases in the 75% PS:25% HDPE may also be responsible for the equivalent or lower creep speed of 75% PS:25% HDPE compared with pure PS [Fig. 3.2B].

Glass Transition Temperatures (T_g)

The T_g of PS was higher in the extruded samples of 50% PS:50% HDPE than in the compression-molded samples (Fig. 3.6). The PS glass transition was also much more obvious in the compression-molded sample. These differences diminished after a second DSC run of the extruded sample. We conclude that annealing took place during the first DSC run, which reduced the difference between compression-molded and extruded samples. These data suggest that the PS was stressed in the extruded samples, presumably from the elongation induced by the processing.
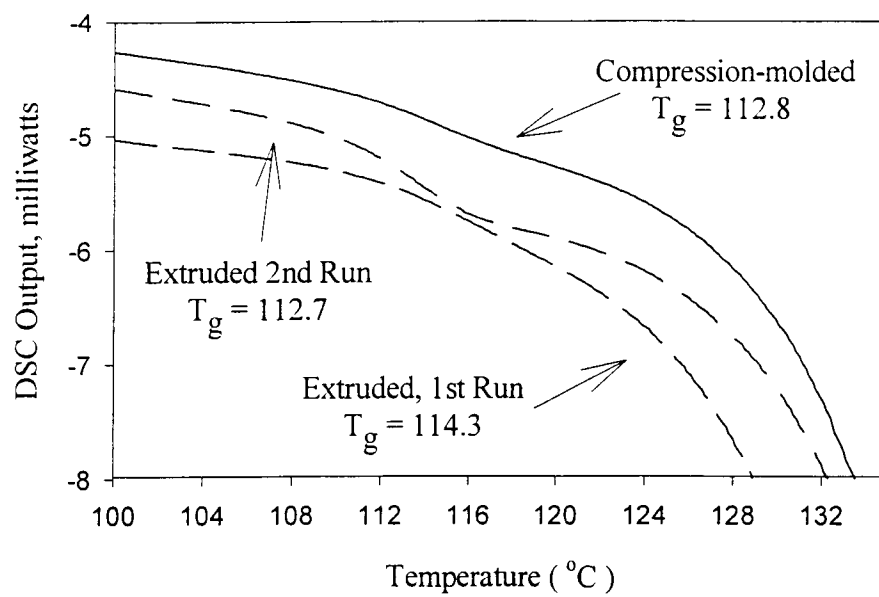
Figure 3.6 DSC Scan of 50%PS:50%PE Samples from Different Processes

Conclusions

The MOE of PS/HDPE blends can be estimated by the weighted average of the MOE values of the components. The strength values of the blends were generally below that expected from a weighted average. The voids in the extruded blends causes the lower density of extruded blends which further account for the lower stiffness.

Processing influence the mechanical properties of the blend considerably. Elongated dispersed PS phases increased the strength of the blend by 50% over that of compression-molded samples, although the MOE is about 25% lower.

Blending PS with HDPE will significantly improve the blends' creep response. It reduces the creep speed from that observed in pure PE, even in pure PS. 50% PS and 75% PS content blends exhibited the best creep resistance. The creep speeds are smaller than pure PS after 500 hours creep test.

Dispersed PS ribbons and droplets were observed in 25% and 75% PS content blend. Intertwined ribbons and droplets were observed in the extruded samples containing 50 or 75% PS. The 75% PS blend showed a co-continuous phase morphology.

Because of a number of reasons, stress existed in the extruded PS and PS/HDPE blends.

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Chapter 4

CREEP RESISTANCE OF WOOD-FILLED
POLYSTYRENE/HIGH-DENSITY POLYETHYLENE BLENDS

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Abstract

Polymer/wood composites have been the subject of much research in recent years, yet problems remain with this class of materials. Low creep resistance is one characteristic of these materials which has resulted in poor performance in certain applications. Improving the creep resistance of these materials might increase the market for products incorporating recycled plastics, especially high density polyethylene (HDPE). This project investigated the feasibility of using blends of low creep resistance HDPE with a plastic of higher creep resistance, polystyrene (PS). Plastic blends of PS/HDPE ratios 25:75, 50:50, 75:25 along with 100%PS and 100%HDPE were used in the studies. The PS/HDPE blends were melt blended with wood flour (short fiber length) in a Banbury mixer and then processed through a single-screw extruder with a slot die attachment. The modulus of elasticity, ultimate stress and creep response of the extruded bars were measured. The creep was determined using a three-point bending geometry with a load of 50% of the ultimate stress. The results showed that creep resistance increased with increasing filler content for most composites. The WF/(75PS-25HDPE) blend showed the best creep resistance. Scanning electron microscope (SEM) images and thermal analysis studies indicated that the wood particles interacted with both the PS and HDPE phases. Although in both cases, the interactions were weak. The PS appeared to have better compatibility with the wood flour than HDPE phase.

Introduction

Wood-filled plastic composites have received a great deal of research interest in recent years and are beginning to find their way into the marketplace[1]. One such product, "plastic lumber," is an alternative for solid wood as a building material. It consists of extruded recycled plastics in the shape of dimension lumber. There are several factors which encourage the appearance of this new material: the increasing demand for building materials, the decreasing availability of quality timber, and the increasing need for new technology to encourage recycling. The lack of a suitable end market for mixed recycled plastics is regarded as the one of the most important factors which hamper plastics recycling[2].

However, compared with solid wood, plastic lumber has poor mechanical properties with the tensile strength and stiffness typically one fourth or less that of solid wood. In addition, the poor creep properties of plastic lumber have led to the need for some in-field replacements in Florida[3]. The low creep resistance (high creep speed) is caused by the low stiffness of the thermoplastics employed, usually which are polyethylene (PE). The mechanical properties of the plastic blends can be improved by adding reinforcing fillers. Wood fiber and flour have been widely used as a reinforcing material in plastic composites, including some plastic lumber products.

Polystyrene (PS) and polyethylene (PE) are two of the most widely used plastics in the world[4]. Their mixture holds the potential for a composite with

mechanical properties which are stronger than HDPE alone, but not as brittle as PS. The morphology and mechanical properties of large dimension extruded PS/HDPE (high density PE) blends have been studied by Li and co-workers[5,6]. In the plastic lumber studied, a morphology gradient were observed and the mechanical properties were evaluated in relationship to the hierarchical morphology. It is reported that the addition of PS increased the stiffness of the blend and suggested the best matrix composition was 35%PS-65%HDPE[7]. The interaction between the wood filler pretreated with phenol-formaldehyde resins and PS/HDPE blends in the compression-molded PS/HDPE/Wood composites has been previously studied in this laboratory[8].

Creep in thermoplastics is a complex phenomenon, depending both upon material properties (molecular orientation, crystallinity, etc[9].) and external parameters (applied stress, temperature, and humidity). The inclusion of wood fibers introduces several additional parameters which effect the mechanical and creep behavior of the composites. These parameters include the fiber volume fraction, the fiber aspect ratio, the orientation of fibers as a result of processing, fiber mechanical properties.

The objective of this study was to investigate the feasibility of increasing the creep resistance of PS/HDPE blends through the addition of wood flour filler and extrusion techniques. The mechanical properties and creep response of various PS/HDPE/WF composites were studied. Scanning electron microscopy (SEM) and

differential scanning calorimetry (DSC) were used to characterize these PS/HDPE/WF composites.

Experimental

Materials

HDPE was contributed by Phillips Petrochemical Company (Houston, Texas) as Marlex EHM 6007. Manufactures specifications give the molecular weight was 120,000 (by gel permeation chromatography); the density, 0.964 g/cm^3; and the melt index, 0.65 g/10 min (190°C/2 kg). Polystyrene (PS) was contributed by Dow Chemical Corporation (Midland, MI) as Dow 685D. The weight-average molecular weight was approximately 300,000; the density, 1.04 g/cm^3; and the melt index, 1.5 g/10 min (200°C/5 kg).

Wood flour (WF) (60-80 mesh) was contributed by Natural Fiber Composites, Inc., (103 Water Street, P.O.Box 138, Baraboo, WI 53913). The aspect ratio of the wood flour was analyzed using a microscope with an Image Analysis System, (NIH Image Version 1.6). More than 300 randomly selected fibers were measured with a resulting aspect ratio (L/D) of 3.0 with a standard deviation of 1.6. The wood flour was dried in a vacuum oven at 60°C overnight before being processed.

Preparation of PS/HDPE/WF Composites

The composites were prepared in two steps. Preliminary mixing was carried out in a Banbury mixer pre-heated to 135°C. 260 grams of either PS, HDPE or blends (25:75, 50:50, 75:25 PS:HDPE) and 160 grams of wood flour were blended in the mixing bowl for 4 minutes. This gave a 40(wt.)% wood flour stock composite. After grinding and passing through a 6mm mesh screen, the composites were dried in a vacuum oven at 60°C overnight before further processing.

The 40% WF:60% plastic mixture prepared above was then diluted with either 100%PS, 100%HDPE or one of the PS/HDPE blends to yield the various wood fiber/plastic mixtures (10, 20, 30 wt.%WF). This mixture was then extruded through a standard 19mm (3/4-in.) single-screw Brabender extruder attached to a Brabender Plastic drive unit. The Brabender extruder was operated at 40 rpm, with the barrel temperature set at 170°C for all heating zones. The melt temperature in the die region was measured as 180°C. A rectangular die (2 × 12 mm) was attached to the extruder. The melt pressures measured at the entrance to the die were in the range of 1 to 3.5MP, depending on the material extruded. A typical extrusion rate was 1.2 m/min. To compensate for the die swell, a shaping die was placed 5–8 cm downstream of the extrusion die. Water was used to cool and solidify the extrudate at the shaping die. A puller was placed downstream from the shaping die and manually synchronized with the extruder to minimize the sag in the melt

extrudate as it exited the rectangular die. The extruded samples were dried in a vacuum oven at 60°C for about 4 hours. Test bars (1.9×11×60 mm) were cut from the cooled extrudate and chosen randomly for testing.

Testing and Characterization

The mechanical testing, creep experiments, rheological testing, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) characterization were performed as described previously[10]. To characterize the role of PS in interaction with the fibers, toluene (good solvent for PS, non-solvent for HDPE) was used to extract the PS from selected samples of the composites. The extraction procedure was described in a previous work[10], but essentially consisted of taking machine and transverse direction section of the extruded bars and extracting them in toluene at room temperature for 4 days with gentle stirring.

Results and Discussion

Mechanical Properties

For all composites,the MOE (modulus of elasticity) increased linearly with increasing WF content to about 30(wt.)% (Fig.4.1). There appeared to be a leveling-off of the MOE from 30% to 40% WF content, which was not expected. This may be due to inadequate shear in the mixer and extruder for the higher filler content composites. A similar phenomenon was observed by Yam and coworkers[11]. The effect was more pronounced for higher PS contents, which may reflect the higher melt viscosity of PS compared to HDPE at the extrusion temperature of 180°C (Fig.4.2).

The ultimate stress may be modulus of rupture (MOR), yield strength (YS) or offset yield strength (OYS), depending the different materials tested. The ultimate stress of PS/WF decreased with increasing filler content while the ultimate stress of PE/WF composites increased with increasing filler content (Fig. 4.3). This trend has been reported previously for uncompatibilized PS composites[12]. Various fracture modes were observed for the composites, with offset yield strength (OYS) reported for high HDPE contents. The remaining composites showed either yielding fracture behavior or brittle fracture. Increasing filler content seemed to
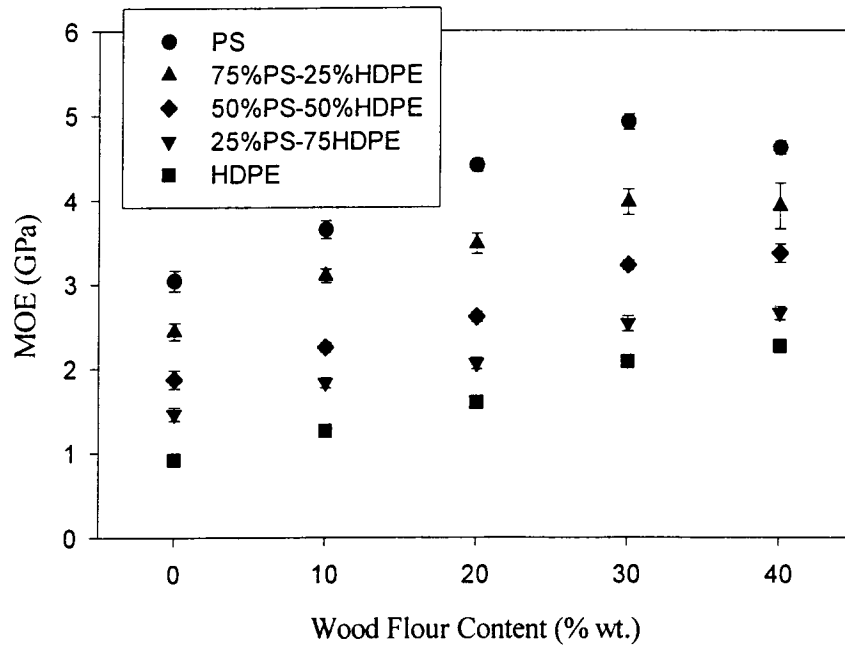
Figure 4.1 The MOE of PS/HDPE/Wood Flour Composites

produce more brittle fracture behavior. The higher PS content, the stiffer the composites (Fig. 4.1), they were also more brittle (Fig. 4.3).

Pure extruded PS did not show brittle fracture. This has been discussed previously[10], and also has been observed by other workers[13]. This may be caused by the stress left inside the sample after the processing, which applied the external forces to PS and then quenched with water. The ultimate stress of the composite increased with increasing PS content, reflecting the stronger, but more brittle, nature of this component. All the composites exhibited an ultimate stress lower than the 100% PS sample.
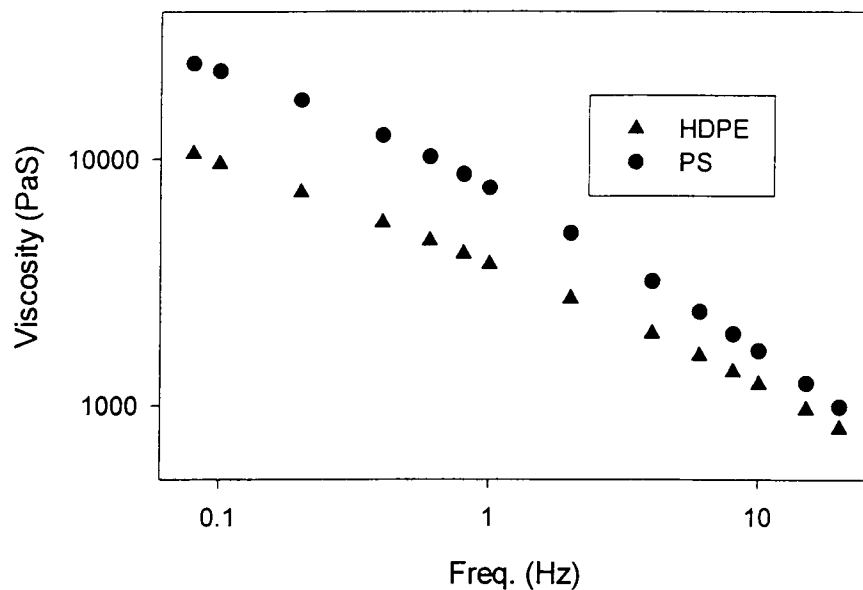
Figure 4.2 Dynamic Viscosity of PS and HDPE at 180°C

Morphology

No WF particles were observed in the SEM images of fractured HDPE/WF

samples (Fig 4.4A). This almost complete "pullout" of the wood filler suggests the

interaction between WF and HDPE was very weak.

In SEM images of PS/HDPE/WF composites not toluene extracted, a thin skin of

HDPE was observed at the surface (Fig. 4.4A). This phenomenon was observed in
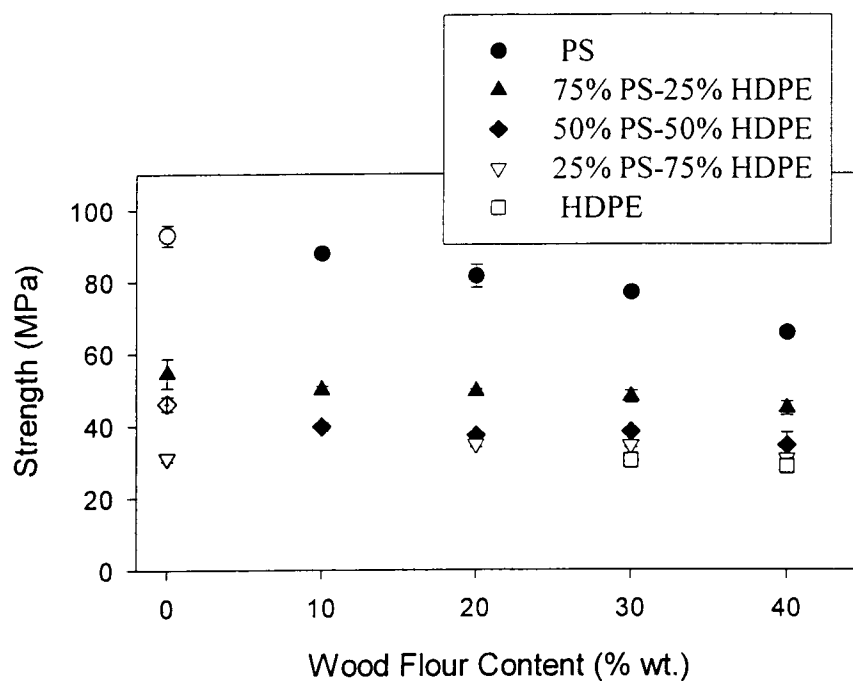
Figure 4.3 The Ultimate Stress PS/HDPE/Wood Flour Composites
(Filled: MOR; unfilled: YS)

previous work and attributed to the low viscosity of HDPE, enhancing its ability to

migrate towards the higher shear wall region of the die. The WF was not uniformly

distributed in the interior of the sample, suggesting that the WF was not well

dispersed by the processing equipment (Banbury mixer and 3/4" single screw

extruder). However, an image at a larger magnification showed that the individual

wood particles were well coated with HDPE (Fig 4.4B). This is to be expected

since the melt state relaxation time of HDPE is about 0.2 second, which is much
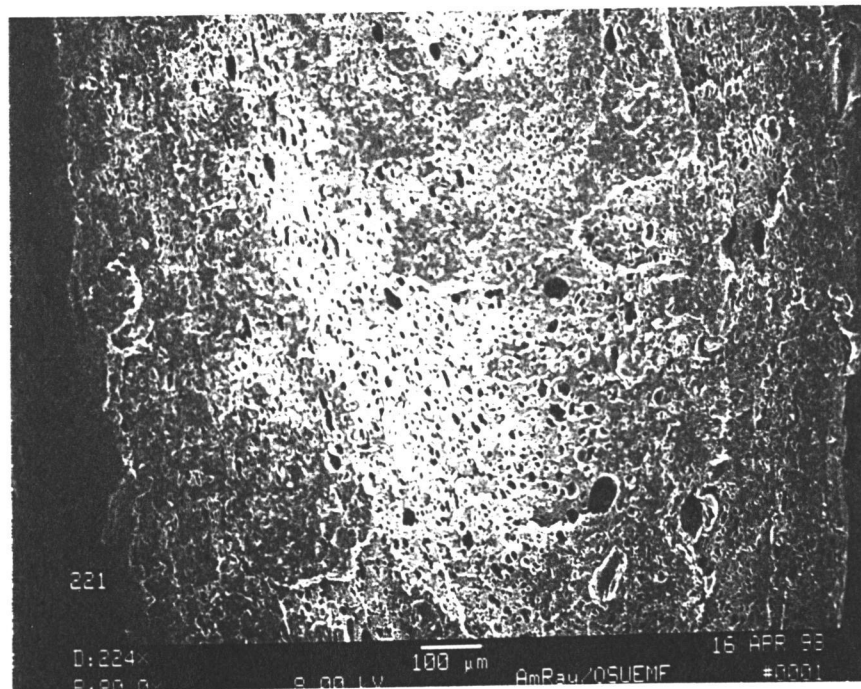
Figure 4.4A SEM of 40%WF-60%HDPE Composites.
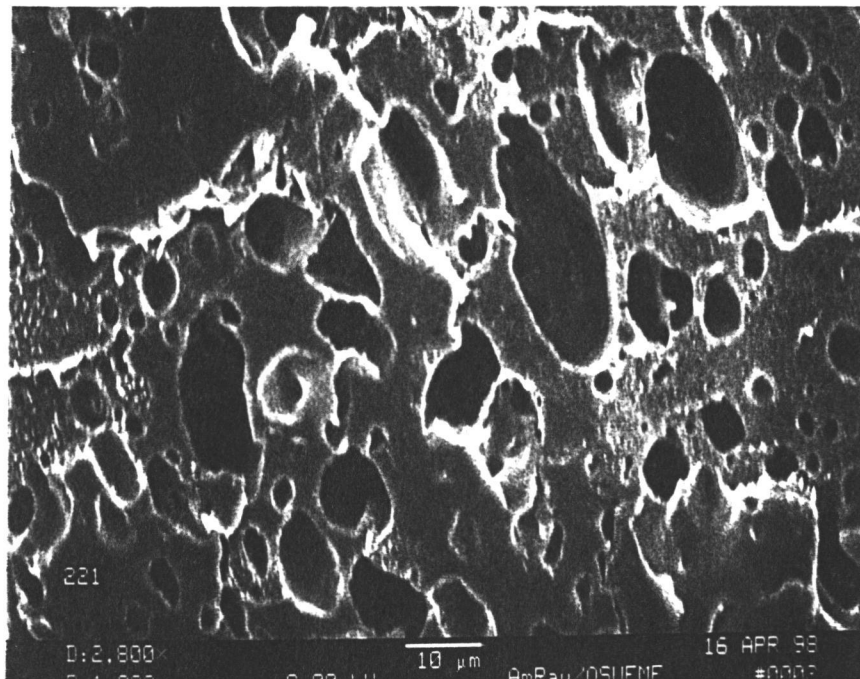
Figure 4.4B. SEM of 40%WF-60%HDPE Composites
in a larger Magnification
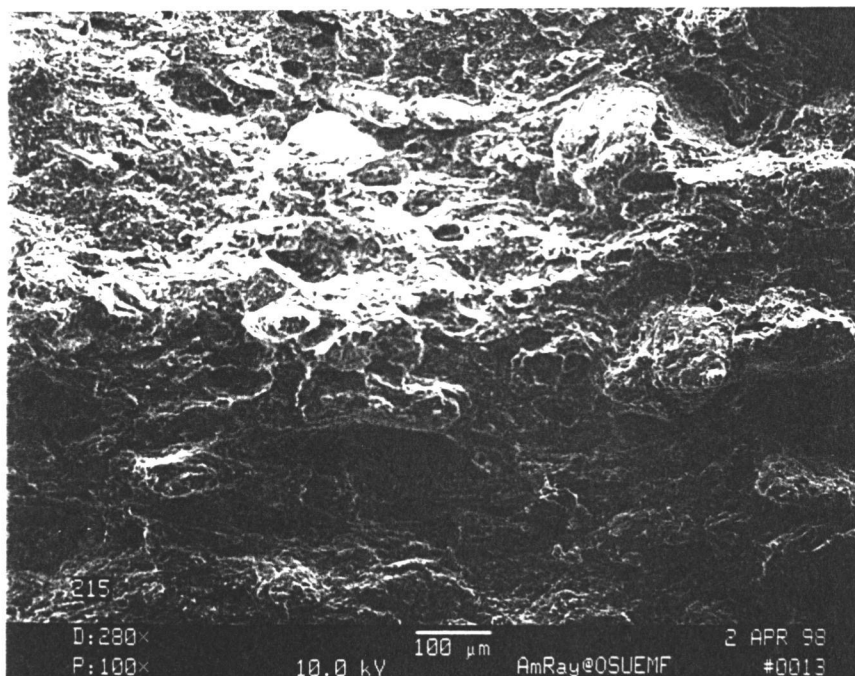
Figure 4.5A SEM of 40%WF:60%(50PS-50HDPE) in Machine Direction
(Without Toluene Treatment)
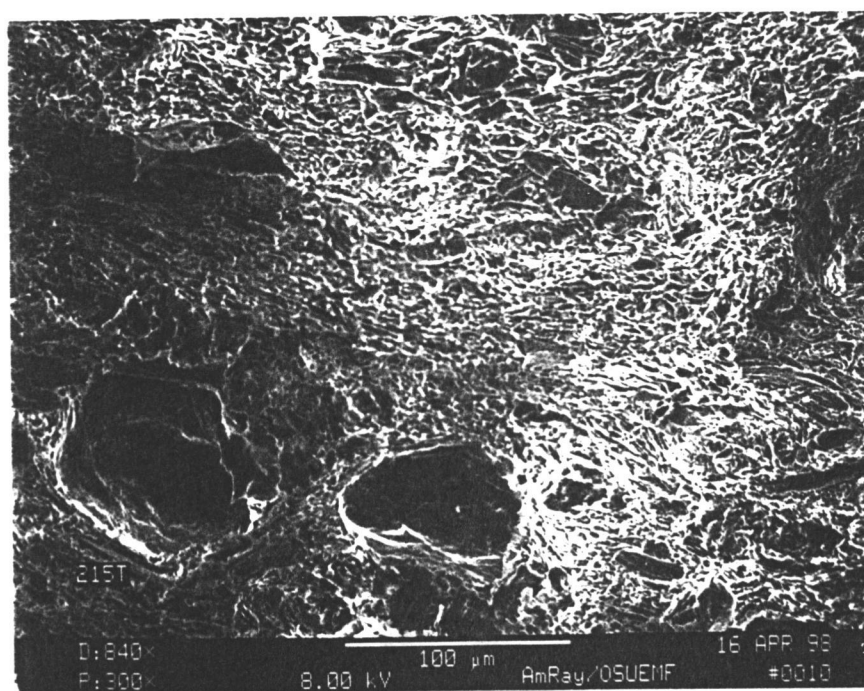
Figure 4.5B SEM of 40%WF:60%(50PS-50HDPE) in Machine Direction
(With Toluene Treatment)
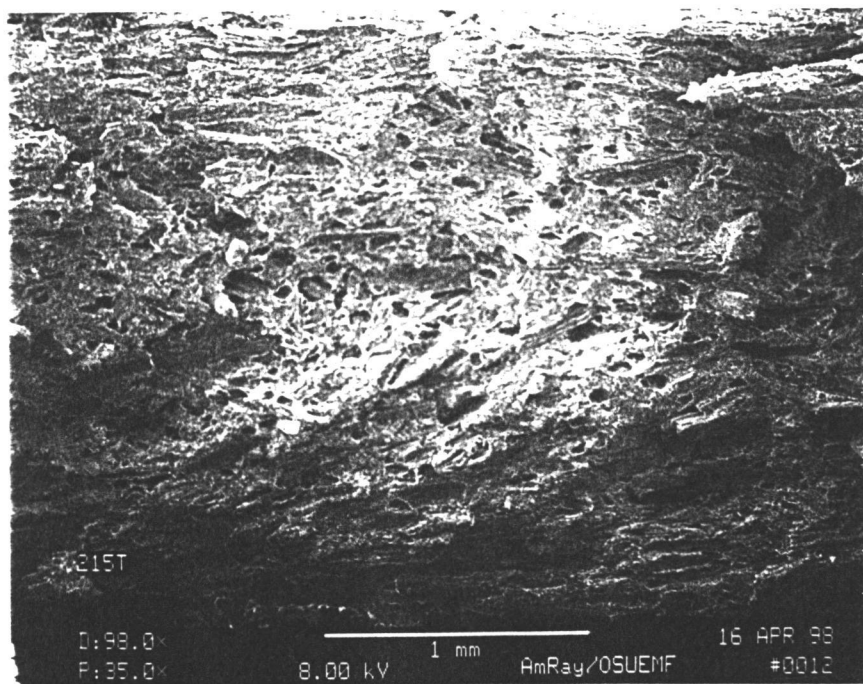
Figure 4.6 SEM of 40%WF-60%(50PS-50HDPE) in Machine Direction

less than the processing time[10], allowing HDPE to thoroughly coat the wood. However, as demonstrated in previous SEM images (Fig. 4.4A), the thorough coating in the melt phase does not lead to a good adherence of HDPE/WF in the solid phase.

The typical size of WF grains observed in the SEM appeared to be smaller than that of unprocessed wood flour, which suggests degradation of the WF during processing. Wood degradation during processing is common and has been previously reported[14].Less fiber "pullout" was observed for the PS/HDPE/WF composites (Fig. 4.5A). Samples from these composites were extracted with

toluene. The resulting SEM images show an almost complete absence of wood particles (Fig.4.5B). This would suggest that the PS coated the wood particles, then when the PS was extracted, the wood particles were removed with PS. If this explanation is accepted, then it would indicate that the wood preferentially adsorbs to PS in PS/HDPE/WF composites. A WF/PS interaction was suggested by previous work[8], and these data would support that hypothesis.

Previous work has shown the presence of a PS ribbon phase for extruded samples at various PS/HDPE ratios[10]. Incorporating 40%WF into similar PS/HDPE blends did not show a similar ribbons phase (Fig.4.6). It can be concluded that the presence of the filler altered the processing characteristics of the blend, resulting in a more separated morphology for the final composite.

Thermal Analysis

DSC spectra indicated that the glass transition temperature (Tg) of the PS phase decreased slightly with increasing filler content (Table 4.1). This is consistent with previous work[15]. This supports the hypothesis that there is a preferential adsorption of PS on the wood filler from PS/HDPE blends.

Table 4.1 Glass Transition Temperature (Tg) of PS in PS/Wood Flour Composites

Wood Flour Content (%)	0	10	20	30	40
Tg (°C)	114.2	113.6	113.4	112.4	112.2
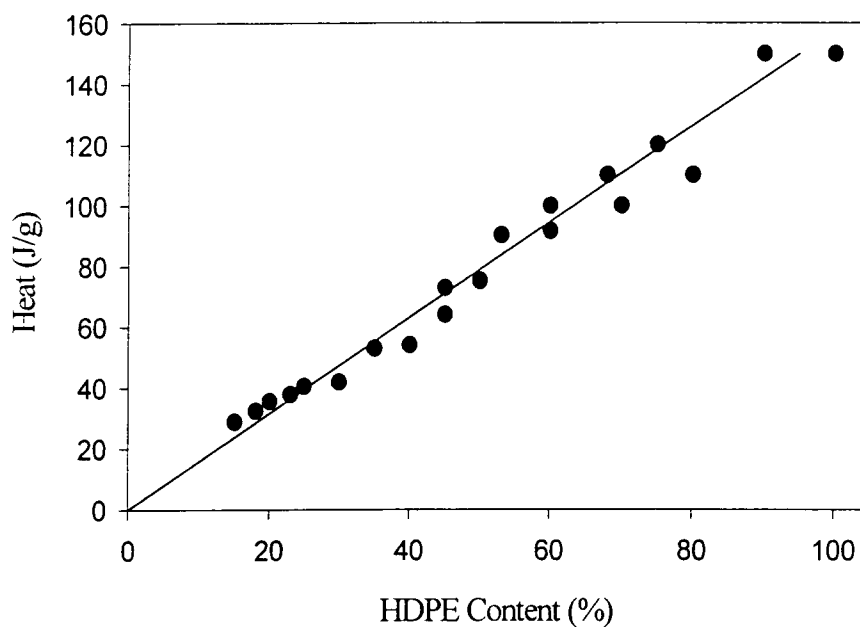
Figure 4.7 The Enthalpy vs. HDPE Content

No interactions between WF and the HDPE phase were observed. DSC spectra indicated that the specific enthalpy (J/g polymer) of the HDPE phase (determined from the integrated area of the melting peak) remained constant regardless of HDPE or WF content (Fig. 4.7). This suggests there is no significant change in the crystallinity of HDPE in the PS/HDPE/WF composite system. Similar results have been obtained in previous work[8,10].

Creep

Following Findley[16], a three parameter empirical power equation was used to model the creep response of the samples (Figs. 4.8- 4.10):

$$\varepsilon = \varepsilon_0 + at^b \qquad (4\text{-}1)$$

where ε is the creep deformation, t is the creep time, and ε_0, a,b are model parameters.

The correlation coefficients for the curve fit are typically >95%, and the standard deviations of the individual a and b parameters are approximately 10% (Table 4.2).

From Fig.4.8-4.10, all the composites having 75%PS:25%HDPE and 50% PS:50% HDPE matrix showed lower creep deformation, even lower than 100%PS matrix. Extruded PS did not break clearly, but yielded, and showed lower stiffness. These process effected material properties may have resulted in the lower creep resistance for 100%PS observed in Fig.3.2A. For 75%PS:25%HDPE, and 50%PS:50%HDPE blends, HDPE was the continuous or co-continuous phase, and the processing conditions were also slightly different, therefore, the stress transferred to dispersed PS phase may have been different from that of the pure PS. This may have resulted in the different creep response observed for these composites.
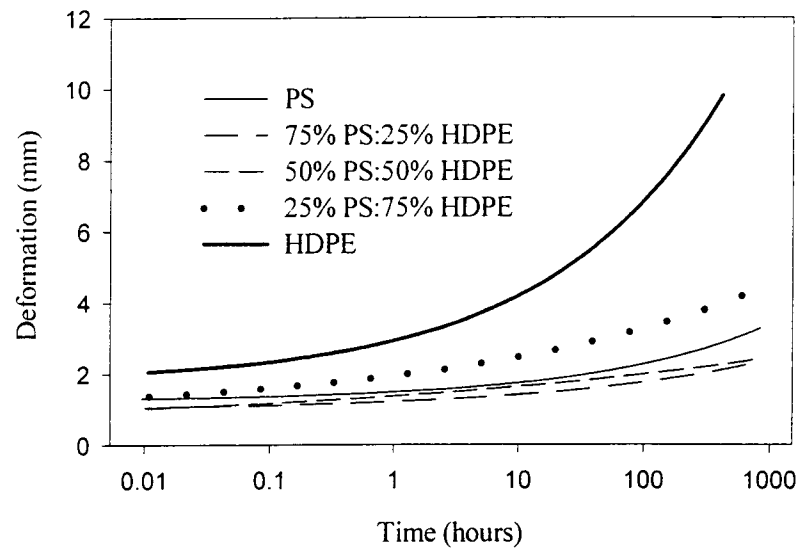
Figure 4.8 Creep Response of 20%WF/80% Plastic Blends
at Various Matrix Composition
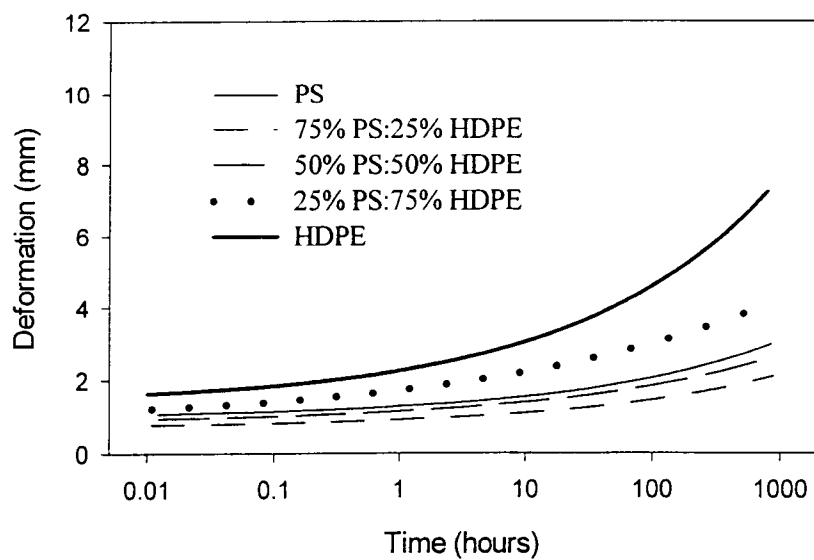
Figure 4.9 Creep Response of 30%WF/70% Plastics Blends
at Various Matrix Composition
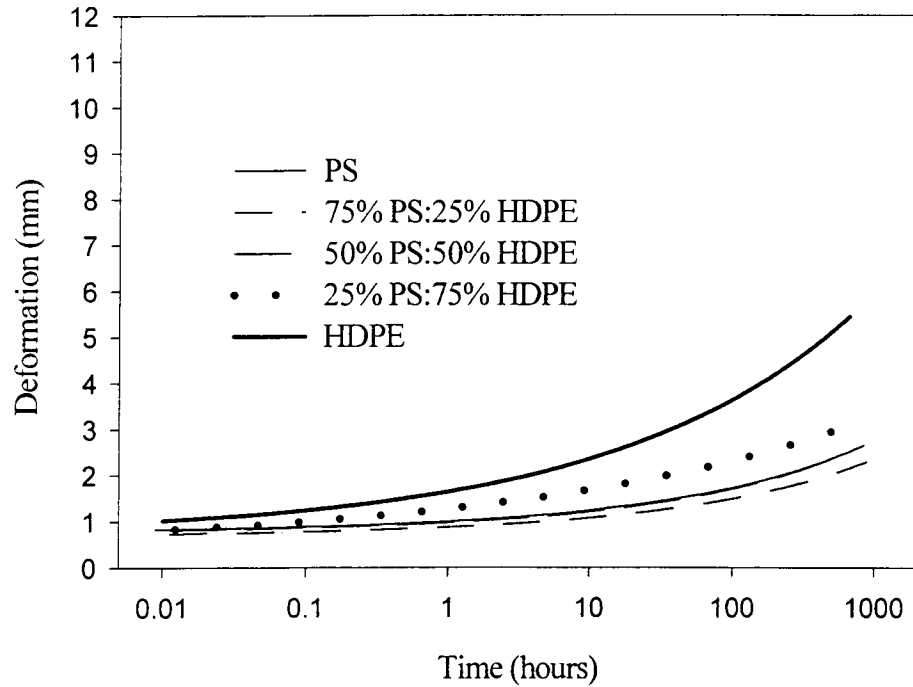
Figure 4.10 Creep Response of 40%WF/60% Plastics Blends
at Various Matrix Composition

Creep speed was derived from equation (4-1) by taking the derivative with

respect to time:

$$V_c = ab \, t^{b-1} \qquad (4\text{-}2)$$

Then ab from equation 4-2 was defined as the "relative creep speed" at unit creep

time.

Creep speed decreased with increasing PS content, except for pure PS (Fig. 4.11), semi-quantifying the observations from the deformation data (Fig. 4.8-4.10). Increasing WF content did lower creep speed, but the extent of the lowering decreased with increasing PS content. One exception to this trend is the 40%WF:60%(75PS-25HDPE) composite. We speculate this anomaly may be due to incomplete blending at the high filler content, but this result requires further study. The effect of WF content on creep speed did not appear to be as large as that of the PS content. This maybe due to the low aspect ratio of the wood fiber used in these studies and the relatively poor blending at the higher filler contents.

Unexpectedly, pure PS showed a lower creep resistance (higher creep speed) than 50% PS:50% HDPE and 75% PS:25% HDPE composites. A similar trend was observed in unfilled blends[10]. This may reflect a change in the morphology of the PS phase due to elongation during processing, although it was shown previously with the SEM images (Fig.4.6) that PS/HDPE/WF composites did not have the ribbon-like morphology of the PS/HDPE blends.

The predominance of PS in controlling creep speed is consistent with the hypothesis that it is the matrix, not the filler, which controls creep in these composites. Thus, the most effective creep reduction strategy lies in altered matrices, not higher filler contents.

Table 4.2. Parameters of the Equation Modeling of Creep Data in PS/HDPE/Wood Composites[Eq. 4-1].
Values are expressed as means (standard error).

Samples	R^2	ε_0	a	b
20%WF:80%PS	0.94	1.26 (0.07)	0.22 (0.05)	0.33 (0.03)
20%WF:80%(75PS-25HDPE)	0.98	0.99 (0.03)	0.22 (0.02)	0.27 (0.01)
20%WF:80%(50PS-50HDPE)	0.88	0.62 (0.31)	0.75 (0.31)	0.13 (0.04)
20%WF:80%(25PS-75HDPE)	0.98	0.95 (0.14)	0.99 (0.13)	0.19 (0.01)
20%WF:80%HDPE	0.98	1.80 (0.22)	1.13 (0.20)	0.32 (0.03)
30%WF:70%PS	0.97	1.01 (0.06)	0.26 (0.04)	0.30 (0.02)
30%WF:70%(75PS-25HDPE)	0.97	0.73 (0.03)	0.18 (0.02)	0.30 (0.02)
30%WF:70%(50PS-50HDPE)	0.97	0.86 (0.06)	0.28 (0.05)	0.27 (0.02)
30%WF:70%(25PS-75HDPE)	0.99	0.89 (0.09)	0.82 (0.09)	0.20 (0.01)
30%WF:70%HDPE	0.98	1.42 (0.14)	0.82 (0.10)	0.30 (0.02)
40%WF:60%PS	0.99	0.78 (0.02)	0.21 (0.01)	0.32 (0.01)
40%WF:60%(75PS-25HDPE)	0.99	0.69 (0.02)	0.18 (0.02)	0.32 (0.01)
40%WF:60%(50PS-50HDPE)	0.98	0.77 (0.04)	0.20 (0.03)	0.34 (0.02)
40%WF:60%(25PS-75HDPE)	0.99	0.51 (0.10)	0.76 (0.09)	0.19 (0.02)
40%WF:60%HDPE	0.94	0.75 (0.20)	0.88 (0.17)	0.26 (0.03)
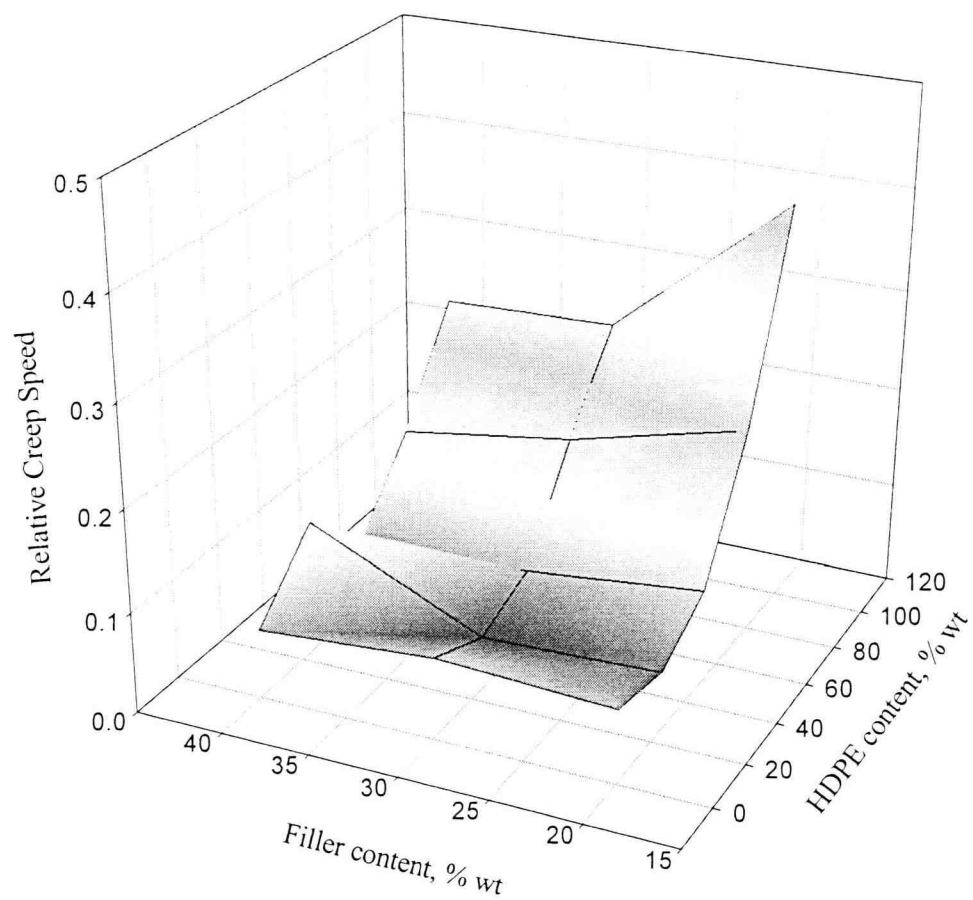
Figure 4.11 Creep Speed of PS/HDPE/Wood Composites
at unit (1 hour) Creep Time

Conclusions

PS/HDPE/WF composites can be blended to produce a controllable range of stiffness and fracture behaviors. The stiffness generally increases with the increasing of PS and WF content.

SEM images and DSC measurement of glass transition temperature indicated that PS phase were found to preferentially adsorb to the wood filler phases, while HDPE adequately coats the wood filler in the melt phase, there is no evidence of adhesion in the solid phase. The further work to improve these interface bonding would be essential. Considering the interaction between any two components in this PS/HDPE/WF composite system, improving the compatibilization of any two components would be beneficial, though, directly attack the HDPE/WF seems to be the most effective.

The creep of this system can be successfully modeled with an empirical three-parameter power model. The creep speed is reduced with increasing PS content, and to a lesser extent, with increasing WF content. The PS/HDPE/WF composites with 50%PS:50%HDPE or 75%PS:25%HDPE plastic matrix show better creep resistance comparing with pure PS matrix, which may due to the changes in the morphology.

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Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

PS/HDPE Blends

The MOE of PS/HDPE blends can be estimated by the weighted average of the MOE values of the components. The strength values of the blends were generally below that expected from a weighted average. The voids in extruded blends leads to a lower density which further accounts for the decreased stiffness.

Processing influences the mechanical properties of the blend considerably. An elongated dispersed PS phase in the extruded blend increased the strength by 50% above that of compression-molded samples, although the MOE was about 25% lower.

A bimodal PS phase distribution consisting of intertwined ribbons and droplets was observed in the extruded samples containing 50 or 75% PS. HDPE was the continuous phase in blends of up to 75%PS. Co-continuous phases were observed in 75%PS:25%HDPE blends.

Creep resistance in PS/HDPE blends can, with some exceptions, be increased by increasing the PS content. 50% PS:50% PE and 75% PS:25% PE

showed a higher creep resistance than 100% PS when tested at 50% of the ultimate stress. The use of blended PE/PS in "plastic lumber" products may improve the mechanical properties and creep resistance.

PS/HDPE/WF Composites

The PS/HDPE/wood flour composites exhibit changes in modulus of elasticity (MOE) and ultimate stress (strength) with component and filler composition. A definitive modulus of rupture (MOR), yield stress or offset yield stress, all measures of the ultimate stress for materials with differing mechanical behavior, can be obtained in the composites. The component composition and processing history both have an effect on the ultimate stress.

In general, MOE increases with increasing wood flour content, as would be expected for the addition of a non-compatible filler material. MOE also increased with increasing PS content due to the higher MOE of PS. The ultimate stress increases slightly with increasing wood flour content for "HDPE-rich" composites, up to about 30wt.% WF. Poor fiber distribution (poor mixing) causes decreases at higher WF levels. The ultimate stress decreases with increasing wood flour content for "PS-rich" composites, and most dramatically for the pure PS composites. This is to be expected for materials such as PS that typical exhibit brittle fracture mechanics. The increasing WF content not only reduces the ultimate stress but changes the nature of the fracture from yielding to brittle for extruded samples.

SEM images of the composites show that HDPE adequately coats the wood flour in the melt state (due to the relative fluidity of HDPE to PS at the melt processing temperature), but that there is little adherence of HDPE to wood flour in the solid state. SEM images of toluene extracted PS/HDPE/WF composites indicate that the wood flour does preferentially adsorb to the PS. However, the strength of the PS/WF interaction can not be determined, and may also be relatively weak. The SEM images also indicate that the aspect ratio of the wood flour may be reduced in processing from its initial L/D=3.0±1.6. Since the filler aspect ratio can have a significant effect on mechanical properties, this is an area of concern which should be further investigated.

Previous studies with PS/HDPE blends indicated a "ribbon-like" PS phases in extruded blends which was not observed in the PS/HDPE/WF composites. The wood flour disrupts the structure development which proved to be beneficial for improving ultimate stress in the PS/HDEP blends. This is to be expected with the addition of any filler.

The creep in these composite systems has been evaluated with a three-parameter power model. Using this model, the creep speed can be determined. The primary goal is a reduction in creep speed. The creep speed is reduced with increasing PS content and , to a lesser extent, with increasing wood flour content. Composites using 75%PS-25%HDPE blend mixed with varying %WF exhibited the lowest creep speed (largest creep resistance). This result is encouraging,

indicating that PS/HDPE/WF composites may indeed produce increased properties as compared to either of the pure component materials (PS or HDPE). Further studies using compatibilizers to increase the HDPE and PS adherence to the wood flour, as well as higher aspect ratio wood flour, are suggested from these results.

Recommendations

The results of the PS/HDPE blends and PS/HDPE/WF composite studies presented in this work indicate several areas for future study:

1. It is desirable to increase the interaction between the components in the PS/HDPE/WF composite system. Compatibilizers that increase both the PS/WF and HDPE/WF adhesion should be investigated.

2. Improved processing techniques to increase filler dispersion should be investigated.

   Suggestions would be to add static mixers to the extruder just prior to the die, and to replace the single-screw extruder with a twin-screw extruder.

3. Wood filler with a larger aspect ratio than the wood flour used in this studies (L/D =3.0) should be used in the composite matrix. A higher aspect ratio filler would be more effectively oriented in the processing stage, which should lead to increased mechanical properties.

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APPENDIX

A.1 Data Repeatability

The data repeatability was carried out by 20%WF:80%(50PS-50HDPE) composite

processing. Two independent composite processes were performed. Table A.1

shows the mechanical properties measured.

Table A.1 The Data Repeatability of Experimental Results
for 20%WF-80%(50PS-50HDPE) Composites

	Sample 1 (BX80)		Sample 2 (BX962)	
	MOE(GPa)	MOR(MPa)	MOE(GPa)	MOR(MPa)
	2.67	38.5	2.54	37.7
	2.57	37.1	2.50	37.9
	2.53	36.2	2.65	39.1
	2.65	36.9	2.41	35.6
	2.63	37.2		36.8
Average	2.61	37.2	2.53	37.4
Std. Dev.	0.058	0.83	0.099	1.31

The t-tests have been used to compare the means of MOR, MOE of the two

samples.

null hypothesis: mean 1 = mean 2

Alt. hypothesis: mean 1 ≠ mean 2

For MOR, the p-value of the t-tests is 0.7382, and for MOE, the p-value is 0.1512.

P-values below 0.05 indicate significant difference between the two means. This

demonstrates that there is not a significant difference between the means of the two

samples at the 95.0% confidence level. All the experiments done in this thesis are

repeatable and reliable.

A.2 Sample Preparation and Process Conditions

The operational conditions of the experiment using Brabender extruder has been described previously. The temperature was set at 170°C to avoid serious damage to the wood flour. The process conditions, which had to be determined, are the Banbury mixing time; the RPM of the extruder, and the different mixing procedure is also compared.

Banbury Mixing Time

The Banbury mixer increases the mixing temperature by a fraction. The increased temperature of the blends will result in a decrease of the viscosity of blends, and eventually, achieve a balance at one definite temperature. The determination of the mixing time of the PS/HDPE/WF blends is a trade-off between the wood fiber dispersion and fiber damage in the blend.

The 40%WF:60%PS system was chosen because of its high viscosity and the difficulty of its dispersion.

Table A.2 The Effect of Banbury Mixing Time

Sample	Mixing Time(mins)	MOR(MPa)	Std Dev. (MPa)	MOE (GPa)	Std Dev. (GPa)
I (BX73)	4	65.6	0.6	4.61	0.08
II (BX75)	7	64.1	3.5	4.62	0.08
III (BX74)	10	71.2	2.1	4.81	0.07

Table 2 shows that there is no significant difference in the MOR, MOE results between 4 and 7 minutes mixing time. A further increase in mixing time will result in some increase in MOR and MOE. However, the color of the mixture is much darker than that of the 4 minute blend. The standard mixing time of a Banbury is about 3 - 5 minutes in industry. A 4 minute Banbury mixing time was chosen throughout this thesis.

Extruder RPM

The fiber orientation effects on the composite mechanical properties have been widely observed [1]. It has been commonly expected that the extrusion of composites will result in this orientation. The effect of extrusion speed (RPM) on 20%WF:80%PS composite is shown in Table A.3.

Table A.3 The Effect of Extruder RPM on the Mechanical Properties
(20%WF-80%PS)

Sample	RPM	MOR(MPa)	Std Dev. (MPa)	MOE (GPa)	Std Dev. (GPa)
I (BX91)	40	81.5	3.2	4.41	0.077
II (BX92)	60	78.8	2.5	4.24	0.06

Theoretically, high speed extrusion will result in highly orientated fibers, and eventually increase the strength of the composites [2]. However, from the data in Table 3, no obvious improvement of mechanical properties was observed where the

RPM increased from 40 to 60. This is attributed to the smaller aspect ratio of wood

flour (3.0±1.6).

40 RPM was chosen throughout this study.

Table A.4 Extruder RPM Effect on Mechanical Properties for PS

Sample	RPM	0.5%	Std Dev. (MPa)	MOE(GPa)	Std Dev. (GPa)
I (BX81)	20	89.7	1.8	3.21	0.09
II (BX82)	40	82.3	2.9	3.04	0.12
III(BX83)	60	81.9	4	3.16	0.20

A.3 Experimental Equipment
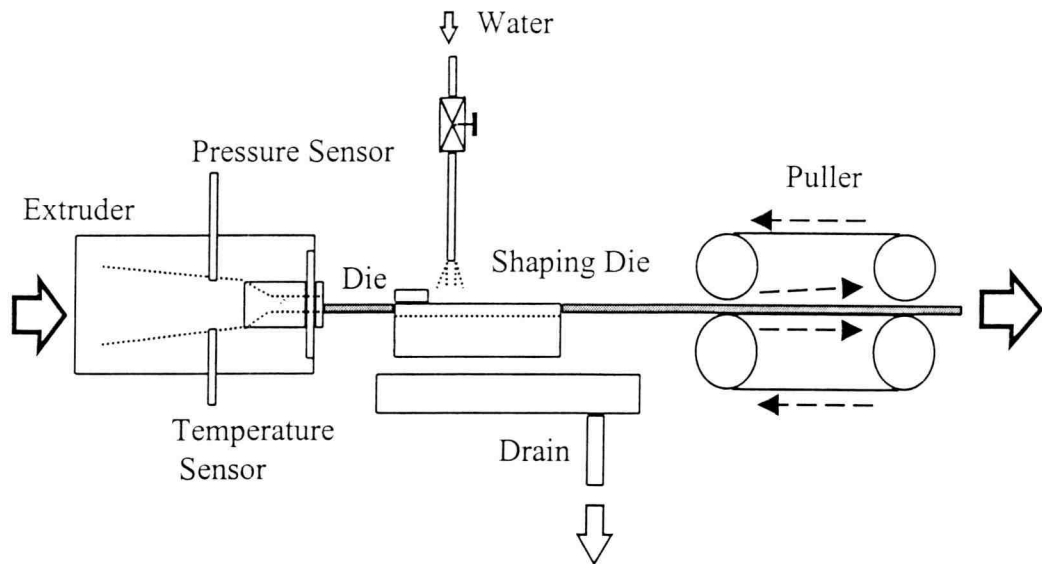
Figure A.1 Extrusion Line
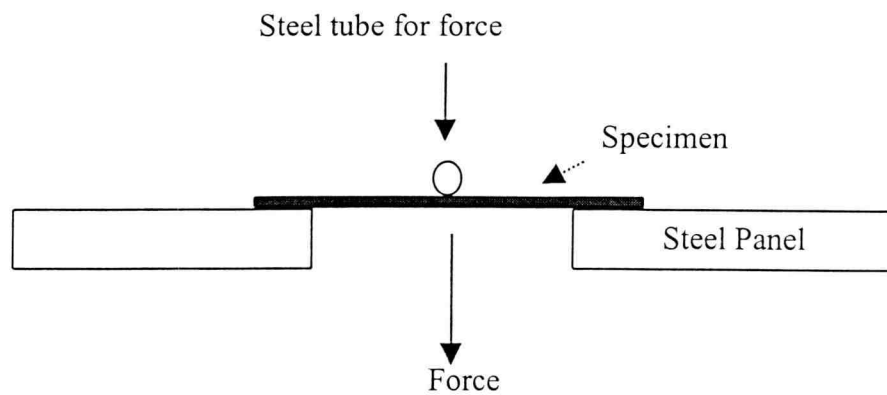
Figure A.2 Creep Experiment Set-up

A.4 Experimental Measurements: Rheological, Mechanical, Thermal and Morphological Characterization

Rheological
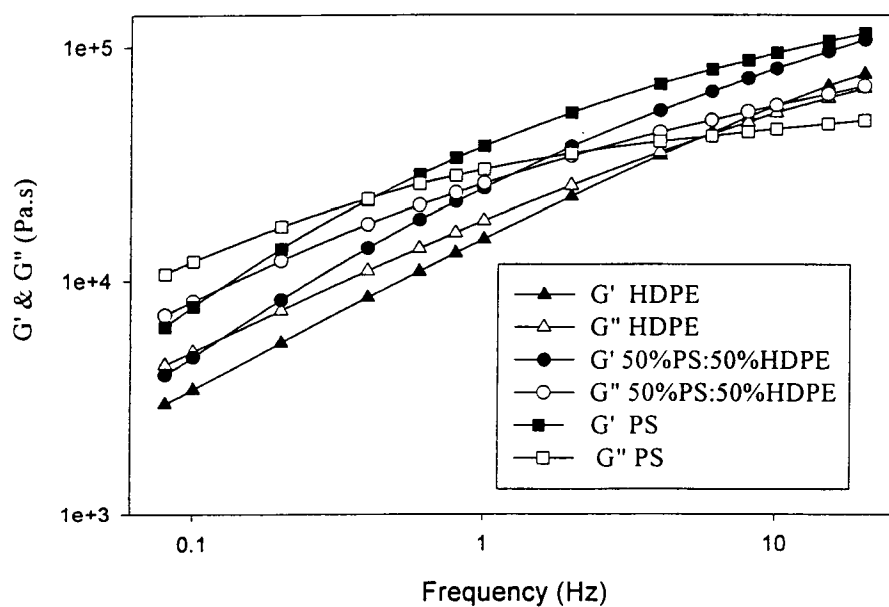
Figure A.3 G', G" of HDPE, PS and 50%PS:50%HDPE Blend

Fig. A.3 is the dynamic oscillatory shear test results. The calculation of relaxation time of polymers has been described in chapter 3.

Mechanical
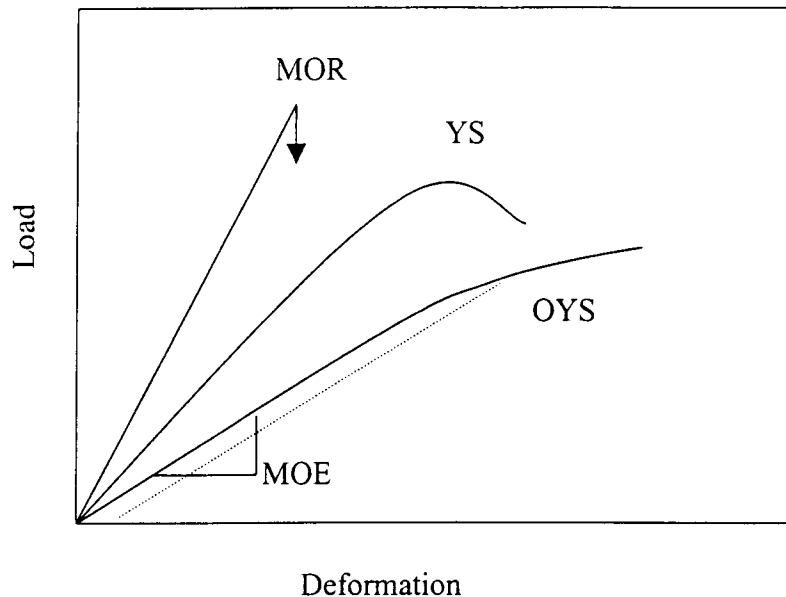
Figure A.4 Schematic Representation of MOE (calculated from the slop)
MOR, YS and OYS

The calculation of MOE, MOR, YS and OYS is described in Chapter 3,

Fig.A.4 is the schematic presentation. From Fig.A.5, the extruded PS show a yield

strength (YS), instead of the MOR. The compression molded 50% PS:50% HDPE

demonstrated the brittle behavior in the stress-strain curve like a compression

molded pure PS, While the extruded samples showed a pure PE-like behavior. The

processing had a significant effect on the final material's performance.
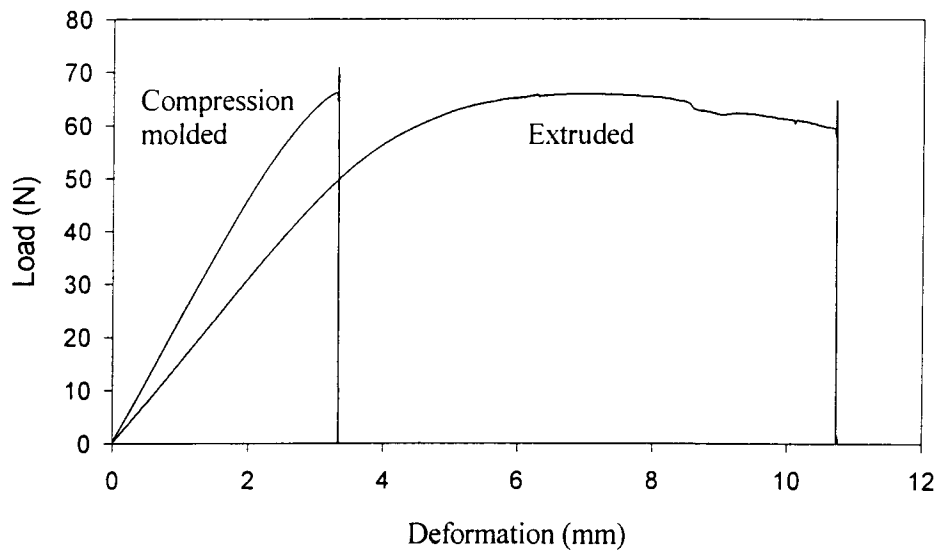
Figure A.5 Stress-Strain Behavior of 100%PS from Dfferent Processes
Extruded (2.1X11.6X56.3mm)
Compression-molded (2.1X12.6X55.0mm)
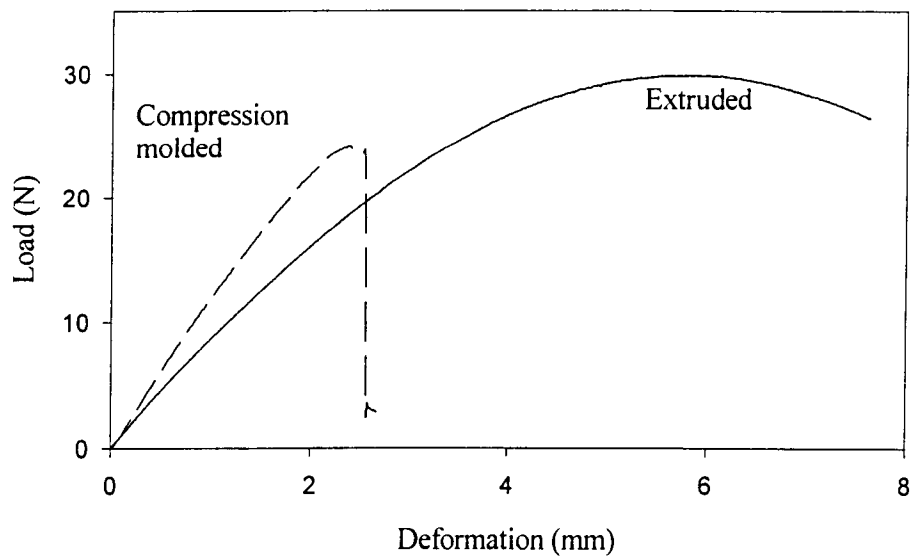
Figure A.6 Comparison of 50% PS:50%PE from Different Processes
Extruded (1.84X11.8X59.4mm)
Compression molded (1.91X12.53X54.5mm)

Thermal
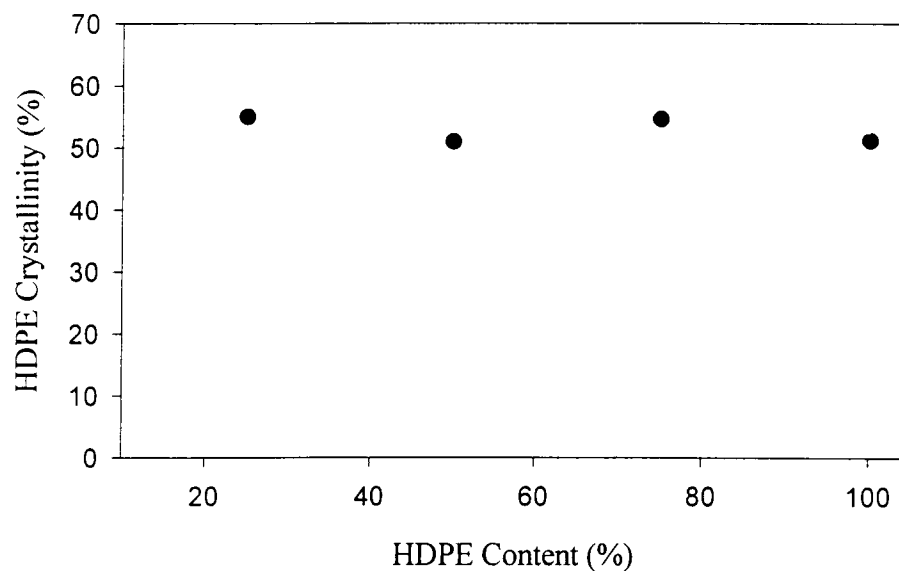
Figure A.7 Crystallinity of HDPE in Extruded PS/HDPE Blends

The crystallinity of HDPE in Fig. A.7 is calculated from the heat absorption

in DSC experiment, divided by the heat absorbed for pure 100%HDPE[3], and then

normalized by the weight percentage in the sample.

Fig. A.8 demonstrated the effect of stress in extruded PS on the DSC

behavior. Because of the stress inside the PS, the PS (1st Run) possessed a wider

glass translation temperature region.
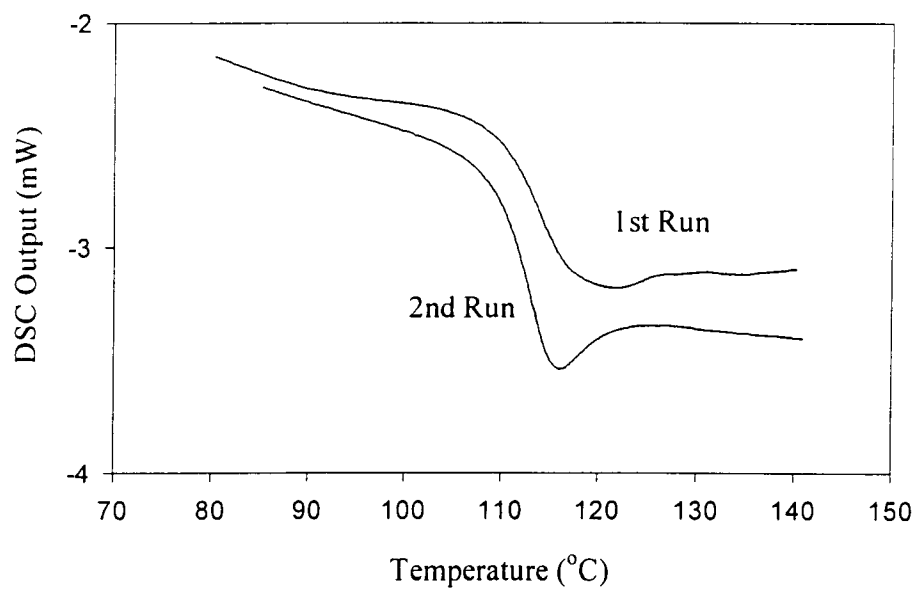
Figure A.8   DSC Experiment Results for Extruded PS

Morphology
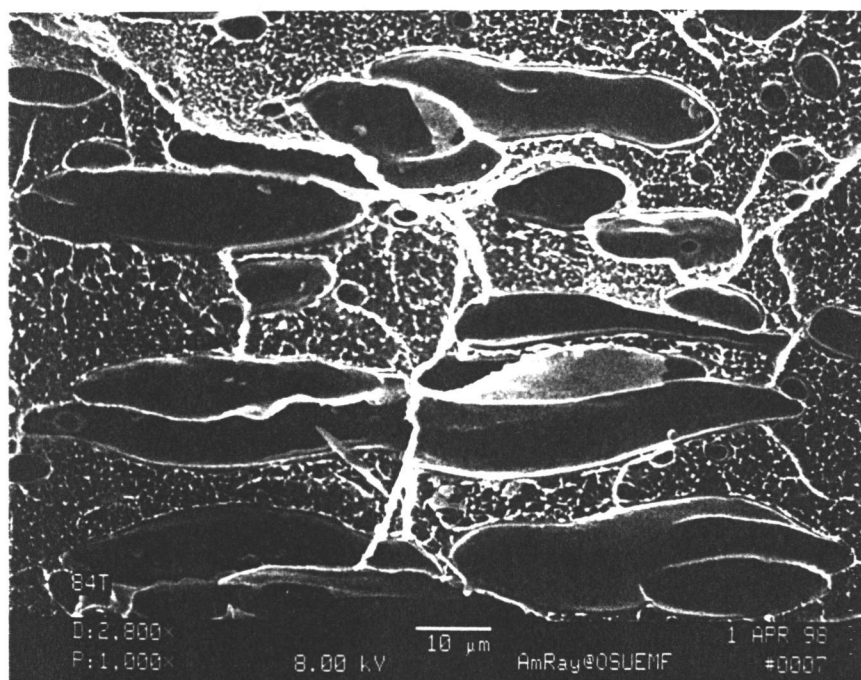
Figure A.9A SEM of 25%PS:75%HDPE blend: Machine Direction
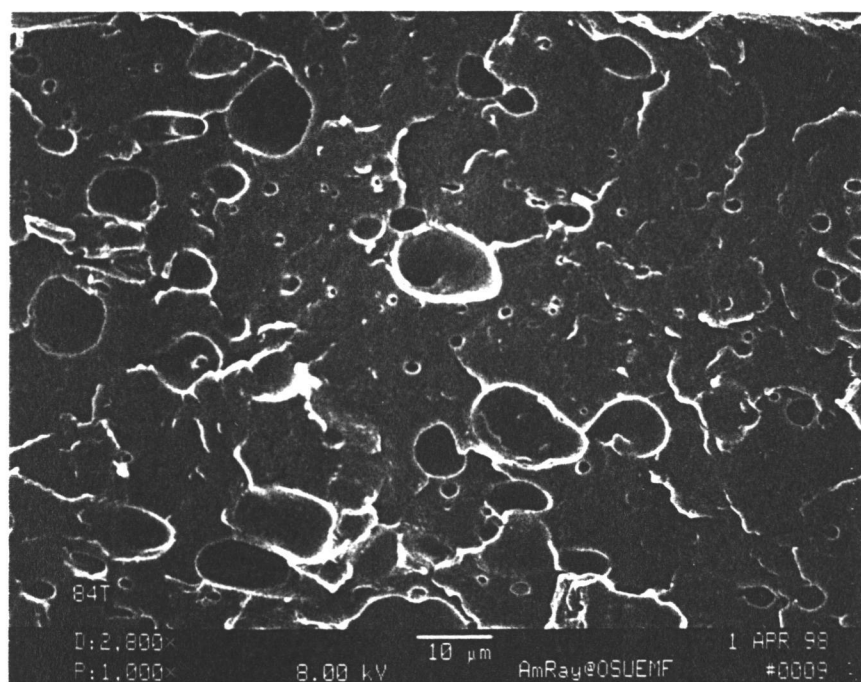
Figure A.9B SEM of 25%PS:75%HDPE: Transverse Direction
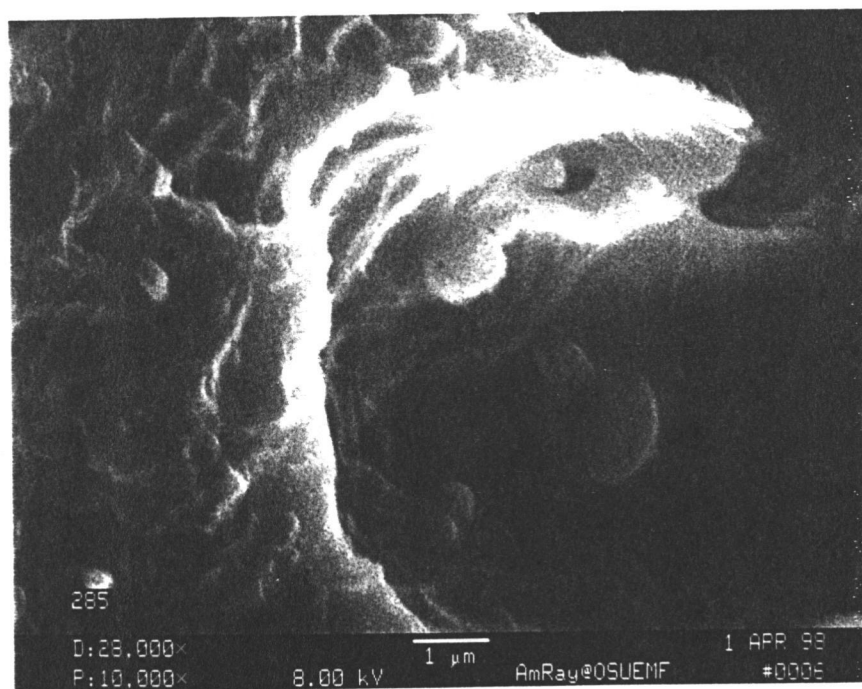
Figure A.10 SEM of Compression-molded 50%PS:50%HDPE Blend
in a larger Magnification

A.5 Creep Data Regression Results

PS

R = 0.99733027   Rsqr = 0.99466766   Adj Rsqr = 0.99451310

Standard Error of Estimate = 0.0512

	Coefficient	Std. Error	t	P
ε_0	2.2527	0.0207	109.0097	<0.0001
a	0.1161	0.0094	12.3413	<0.0001
b	0.4390	0.0115	38.1419	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	33.7419	16.8710	6435.4538	<0.0001
Residual	69	0.1809	0.0026		
Total	71	33.9228	0.4778		

75%PS:25%HDPE

R = 0.93199786   Rsqr = 0.86862002   Adj Rsqr = 0.86585412

Standard Error of Estimate = 0.0458

	Coefficient	Std. Error	t	P
ε_0	1.1217	0.2580	4.3471	<0.0001
a	0.5358	0.2605	2.0566	0.0425
b	0.0683	0.0284	2.4052	0.0181

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	1.3178	0.6589	314.0467	<0.0001
Residual	95	0.1993	0.0021		
Total	97	1.5171	0.0156		

50%PS:50%HDPE

R = 0.97589119   Rsqr = 0.95236362   Adj Rsqr = 0.95089788

Standard Error of Estimate = 0.0614

	Coefficient	Std. Error	t	P
ε_0	1.4655	0.1310	11.1848	<0.0001
a	0.5470	0.1315	4.1598	<0.0001
b	0.1302	0.0223	5.8456	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	4.9062	2.4531	649.7516	<0.0001
Residual	65	0.2454	0.0038		
Total	67	5.1516	0.0769		

25%PS-75%HDPE

R = 0.96835108   Rsqr = 0.93770381   Adj Rsqr = 0.93581605

Standard Error of Estimate = 0.2508

	Coefficient	Std. Error	t	P
ε_0	1.7926	0.2674	6.7031	<0.0001
a	1.0493	0.2511	4.1785	<0.0001
b	0.1959	0.0278	7.0593	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	62.4940	31.2470	496.7274	<0.0001
Residual	66	4.1518	0.0629		
Total	68	66.6458	0.9801		

HDPE

R = 0.98820057   Rsqr = 0.97654037   Adj Rsqr = 0.97609774

Standard Error of Estimate = 0.2702

	Coefficient	Std. Error	t	P
ε_0	0.1270	0.4065	0.3124	0.7554
a	3.2045	0.4005	8.0007	<0.0001
b	0.1395	0.0119	11.7007	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	322.1007	161.0504	2206.2002	<0.0001
Residual	106	7.7379	0.0730		
Total	108	329.8386	3.0541		

50%PS:50%HDPE Compression-molded

R = 0.99106770   Rsqr = 0.98221518   Adj Rsqr = 0.98171420

Standard Error of Estimate = 0.0308

	Coefficient	Std. Error	t	P
ε_0	-1.4921	1.1297	-1.3208	0.1908
a	2.8619	1.1328	2.5263	0.0138
b	0.0273	0.0109	2.5076	0.0144

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	3.7195	1.8598	1960.5843	<0.0001
Residual	71	0.0673	0.0009		
Total	73	3.7868	0.0519		

30% WF:70% PS

R = 0.98422797   Rsqr = 0.96870469   Adj Rsqr = 0.96781054

Standard Error of Estimate = 0.1003

	Coefficient	Std. Error	t	P
ε_0	1.0110	0.0590	17.1405	<0.0001
a	0.2602	0.0434	5.9976	<0.0001
b	0.2993	0.0220	13.6047	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	21.7879	10.8940	1083.3785	<0.0001
Residual	70	0.7039	0.0101		
Total	72	22.4918	0.3124		

30%WF:70%(75PS-25HDPE)

R = 0.98519561   Rsqr = 0.97061040   Adj Rsqr = 0.97006614

Standard Error of Estimate = 0.0654

	Coefficient	Std. Error	t	P
ε_0	0.7303	0.0318	22.9663	<0.0001
a	0.1816	0.0234	7.7502	<0.0001
b	0.2969	0.0170	17.4588	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	15.2349	7.6175	1783.3843	<0.0001
Residual	108	0.4613	0.0043		
Total	110	15.6962	0.1427		

30%WF:70%(50PS-50HDPE)

R = 0.98398339   Rsqr = 0.96822331   Adj Rsqr = 0.96716409

Standard Error of Estimate = 0.0845

	Coefficient	Std. Error	t	P
ε_0	0.8613	0.0578	14.8973	<0.0001
a	0.2776	0.0471	5.8926	<0.0001
b	0.2715	0.0225	12.0731	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	13.0480	6.5240	914.0884	<0.0001
Residual	60	0.4282	0.0071		
Total	62	13.4762	0.2174		

30%WF:70%(25PS-75HDPE)

R = 0.99263017   Rsqr = 0.98531465   Adj Rsqr = 0.98486964

Standard Error of Estimate = 0.0985

	Coefficient	Std. Error	t	P
ε_0	0.8917	0.0898	9.9270	<0.0001
a	0.8195	0.0869	9.4283	<0.0001
b	0.2044	0.0132	15.5333	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	42.9620	21.4810	2214.1378	<0.0001
Residual	66	0.6403	0.0097		
Total	68	43.6024	0.6412		

30%WF:70%HDPE

R = 0.98745490 Rsqr = 0.97506718 Adj Rsqr = 0.97459227

Standard Error of Estimate = 0.2620

	Coefficient	Std. Error	t	P
ε_0	1.4210	0.1370	10.3723	<0.0001
a	0.8178	0.1007	8.1179	<0.0001
b	0.2950	0.0163	18.1330	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	281.7768	140.8884	2053.1587	<0.0001
Residual	105	7.2051	0.0686		
Total	107	288.9820	2.7008		

20%WF:80%PS

R = 0.97002707 Rsqr = 0.94095251 Adj Rsqr = 0.93959510

Standard Error of Estimate = 0.1506

	Coefficient	Std. Error	t	P
ε_0	1.2575	0.0661	19.0118	<0.0001
a	0.2233	0.0455	4.9073	<0.0001
b	0.3271	0.0279	11.7151	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	31.4516	15.7258	693.1952	<0.0001
Residual	87	1.9737	0.0227		
Total	89	33.4253	0.3756		

20%WF:80%(75PS-25HDPE)

R = 0.99238500   Rsqr = 0.98482799   Adj Rsqr = 0.98453622

Standard Error of Estimate = 0.0452

	Coefficient	Std. Error	t	P
ε_0	0.9883	0.0254	38.9131	<0.0001
a	0.2232	0.0202	11.0482	<0.0001
b	0.2670	0.0116	23.0700	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	13.7755	6.8878	3375.3648	<0.0001
Residual	104	0.2122	0.0020		
Total	106	13.9878	0.1320		

20%WF:80%(50PS-50HDPE)

R = 0.93732664   Rsqr = 0.87858123   Adj Rsqr = 0.87372448

Standard Error of Estimate = 0.1446

	Coefficient	Std. Error	t	P
ε_0	0.6160	0.3102	1.9860	0.0525
a	0.7493	0.3106	2.4122	0.0196
b	0.1298	0.0389	3.3327	0.0016

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	7.5677	3.7839	180.8990	<0.0001
Residual	50	1.0459	0.0209		
Total	52	8.6136	0.1656		

20%WF:80%(25PS-75HDPE)

R = 0.99055073   Rsqr = 0.98119074   Adj Rsqr = 0.98062927

Standard Error of Estimate = 0.1192

	Coefficient	Std. Error	t	P
ε_0	0.9513	0.1376	6.9131	<0.0001
a	0.9864	0.1304	7.5658	<0.0001
b	0.1859	0.0147	12.6285	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	49.6760	24.8380	1747.5376	<0.0001
Residual	67	0.9523	0.0142		
Total	69	50.6283	0.7337		

20%WF:80%HDPE

R = 0.98807802   Rsqr = 0.97629818   Adj Rsqr = 0.97522083

Standard Error of Estimate = 0.4017

	Coefficient	Std. Error	t	P
ε_0	1.8003	0.2470	7.2894	<0.0001
a	1.1334	0.1961	5.7800	<0.0001
b	0.3244	0.0257	12.6003	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	292.4946	146.2473	906.1988	<0.0001
Residual	44	7.1010	0.1614		
Total	46	299.5955	6.5129		

40%WF:60%PS

R = 0.99737139   Rsqr = 0.99474969   Adj Rsqr = 0.99465155

Standard Error of Estimate = 0.0388

	Coefficient	Std. Error	t	P
y0	0.7811	0.0171	45.5500	<0.0001
a	0.2135	0.0118	18.0974	<0.0001
b	0.3221	0.0074	43.2482	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	30.5257	15.2629	10136.3748	<0.0001
Residual	107	0.1611	0.0015		
Total	109	30.6868	0.2815		

40%WF:60%(75PS-25HDPE)

R = 0.99388991   Rsqr = 0.98781715   Adj Rsqr = 0.98759361

Standard Error of Estimate = 0.0501

	Coefficient	Std. Error	t	P
ε_0	0.6883	0.0221	31.1273	<0.0001
a	0.1806	0.0151	11.9956	<0.0001
b	0.3217	0.0112	28.7104	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	22.1583	11.0791	4419.0025	<0.0001
Residual	109	0.2733	0.0025		
Total	111	22.4316	0.2021		

40%WF:60%(50PS-50HDPE)

R = 0.98936816   Rsqr = 0.97884936   Adj Rsqr = 0.97815590

Standard Error of Estimate = 0.0769

	Coefficient	Std. Error	t	P
ε_0	0.7702	0.0415	18.5399	<0.0001
a	0.1983	0.0288	6.8758	<0.0001
b	0.3348	0.0204	16.3883	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	16.6859	8.3430	1411.5369	<0.0001
Residual	61	0.3605	0.0059		
Total	63	17.0465	0.2706		

40%WF:60%(25PS-75HDPE)

R = 0.99260733   Rsqr = 0.98526931   Adj Rsqr = 0.98462885

Standard Error of Estimate = 0.0830

	Coefficient	Std. Error	t	P
ε_0	0.5058	0.1016	4.9802	<0.0001
a	0.7571	0.0986	7.6822	<0.0001
b	0.1887	0.0153	12.3515	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	21.1744	10.5872	1538.3664	<0.0001
Residual	46	0.3166	0.0069		
Total	48	21.4910	0.4477		

40%WF:60%HDPE

R = 0.97114497   Rsqr = 0.94312255   Adj Rsqr = 0.94166415

Standard Error of Estimate = 0.3222

	Coefficient	Std. Error	t	P
ε_0	0.7523	0.1976	3.8078	0.0003
a	0.8817	0.1705	5.1703	<0.0001
b	0.2575	0.0259	9.9469	<0.0001

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	134.2661	67.1330	646.6847	<0.0001
Residual	78	8.0973	0.1038		
Total	80	142.3633	1.7795		

A.6. Preliminary Studies of Compatibilizers for the PS/HDPE/Wood fiber Composites

Introduction

An alternative for timber in building materials is "plastic lumber", which is recycled plastic blend extruded in dimensional shapes. Plastic lumber can make up a shortage in timber, encourage plastic recycling, and save resources. Wood filler has been used to improve the mechanical properties of Polystyrene/High Density Polyethylene blends[4,6,7]. However, because of the incompatibility among these three components, the mechanical property enhancement of these composite system is not at a level suitable for commercial utilization. The interfacial bonding between the wood fiber and the plastics is weak, especially for at the wood - high density polyethylene interface[6]. The addition of copolymers to improve the component compatibility has become a common practice, and various copolymers are commercially available. For PS/HDPE/wood fiber composites, the pretreatment of wood filler with phenol-formaldehyde resins has been attempted with limited success[7].

In this brief study, the effect of several copolymers has been investigated for a 35%WF:65%(50PS-50HDPE) composite.

Experimental

The suppliers of the compatibilizing agent are listed in the Table 1. All of the chemicals were used as received. The wood fiber T-14 used in this study has been described else where[5]. The blending, processing, and mechanical testing of the composites have been described in previous work [6]. The PS/HDPE/T-14 blends were mixed in a Banbury mixer first, then processed through single-screw extruder (3/4") with a forming die attached to the end. Extruded bars were then chopped to the appropriate size (1.9×11.5×60mm) for testing. Five specimens of each sample were tested. The data repeatability of the experiment was very good, and there was no significant difference between the mean of the two repeated samples at the 95.0% confident level[9].

Results

Table 1 is a summary of the experimental data. For all samples, the modulus of rupture (MOR) could be calculated.

The additives of G-3002 and G-3003 have been shown to be effective coupling agents for wood fiber with a polypropylene matrix [10]. A statistical method (t-tests) has been applied to the comparison of the mean between sample 2 (or 3) and 1.

null hypothesis: mean a = mean b

Alt. hypothesis: mean a > mean b

P-values below 0.05 indicate a significant difference between the two means.

For the G-3002 additive, the P-value is 0.00087. For the G-3003 additive, the P-value is 0.0038. This analysis demonstrates that there are significant differences between the samples with or without these two bonding agents, and that the samples with the additives have higher MOR than the non-additive sample at 95% confidence level. The effectiveness of these two additives can be attributed to the acid radicals in the additives, and which enhanced the interfacial bonding between the faces of plastics and wood fiber.

Kraton 1901X is a linear styrene-ethylene-butylene-styrene block copolymer (SEBS). SEBS has been effectively used to improve the compatibility of PS/PE blends [11]. The statistical analysis of Kraton 1901X data also shows there is a significant difference between the means of the additive and non-additive samples (P-value: 0.0077).

The dispersion of wood fiber in the HDPE matrix has been reported to be a major concern [12]. Stearic acid has been tried by Woodhams to improve the dispersion [13]. The results of present studies show that the aluminum stearate had a detrimental effect of composite mechanical properties the composite mechanical properties.

All of the current studies have shown that the additives of compatibilizers had no significant effect on the stiffness.

Future studies should be conducted to examine wood fiber dispersion and adherence in the presence of compatibilizers, and to relate this to mechanical properties.

Table A.5 The Effect of additives on the composite MOR, MOE for 35%WF-65%(50PS-50HDPE) Composites. Values are expressed as means (standard error).

Additives	Supplier	Amount based on filler (wt.%)	MOR (MPa)	MOE (GPa)
-	---	0	33.4 (1.1)	2.80 (0.11)
G-3002	Shell Chem. Corp.	4	36.1 (0.9)	2.91 (0.2)
G-3003	Shell Chem. Corp.	4	35.8 (1.3)	2.67 (0.18)
Kraton 1901X	Shell Chem. Corp.	4	35.6 (0.9)	2.67 (0.14)
Epolene Wax C-16	Witco Corp.	4	34.3 (0.4)	2.74 (0.2)
K. W-20 F.B[1]	Witco Corp	3	31.9 (1.1)	2.93 (0.06)
K. W-20 F.B		1	30.1 (1.3)	2.72 (0.09)
Ceramer 1608	Pertrolite Corp.	3	31.0 (0.9)	2.83 (0.13)
Ceramer 1608		1	30.0 (0.3)	2.53 (0.13)
Aluminu Stearate	Pertrolite Corp.	1	32.2 (0.7)	2.83 (0.11)

[1] Kemamide W-20 fatty bisamide

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