

Cowoven Polypropylene/Glass Composites With Polypropylene + Polymer Liquid Crystal Interlayers: Dynamic Mechanical and Thermal Analysis

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Simultaneous macroscopic and molecular reinforcement of polypropylene with glass fibers and Polymer Liquid Crystals (PLCs) is evaluated. Interlayers of polypropylene (PP) + poly(ethylene terephthalate) /0.6 p-hydroxybenzoic acid PLC blends are introduced between the cowoven polypropylene + glass fiber plies. Analysis was conducted using Dynamic Mechanical Thermal Analysis (DMTA), Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA). The results indicate that low fractions of PLC material in the composite have dual benefits of increased rigidity and toughness. The crystallization kinetics are influenced by the dual nucleating effects of both reinforcing agents. A decrease in crystallinity is associated with increasing PLC presence. Degradation kinetics of the composites demonstrate only one kinetic step in contrast to the interlayers alone.

1. INTRODUCTION

Thermoplastic composites made from consumer plastics such as polypropylene become viable structural candidates when reinforced by glass (1). Conventionally manufacture has followed traditional hand lay-up techniques involving alternate layering of matrix layers with glass mat. Alternatives to this process include the "Fiber Impregnated by Thermoplastics" (FIT) process, where the reinforcement is pulled through a thermoplastic powder bed and then extrusion coated to encapsulate the powder (2). Other alternatives include: powder processing technology to electrostatically bond the matrix powder to the fiber; and wet-powder techniques where an aqueous medium is employed to ensure adequate distribution of the powder over the fiber. In contrast to these techniques, we use cowoven glass fiber + polypropylene mats. This eliminates much of the error associated with inadequate matrix distribution across the fiber interface.

Polypropylene (PP) has many advantages as a matrix resin for thermoplastic composites owing to its relatively low cost and high chemical resistance coupled with ease of fabrication. A major limitation of PP is that its glass transition is below room temperature, consequently its dimensional stability is limited.

Efforts to alleviate this problem have included macroscopic reinforcement through the introduction of short glass fibers and glass beads as well as molecular reinforcement by blending it with other engineering thermoplastics. One promising avenue has been the introduction of polymer liquid crystals (PLCs) also known as liquid crystalline polymers (LCPs) (3-5). PLCs are candidates in applications requiring high-performance engineering materials. They possess several advantages over conventional thermoplastic polymer composites with regard to chemical resistance, low flammability, ease of processing, and high modulus (6). In addition, they are much lighter in weight than ceramic reinforcements leading to greater potential for engineering applications. However, they have been so far relatively costly. One way to eliminate the cost advantage is by blending (7). This is not simple. Preserving good PLC properties while diluting it with a (usually flexible) engineering polymer is by no means automatically ensured. One route toward achieving the desired effects appears if their phase diagram shows favorable features in terms of constituent miscibility (8). In the glass reinforced composites a relatively soft polymer matrix is reinforced on a macroscopic scale by the fibers. PLCs on the other hand provide reinforcement at the molecular level; the relatively rigid liquid crystalline sequences are connected to the flexible sequences by primary chemical bonds.

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The stiffening constituent is thus present within each macromolecule. If combined with more inexpensive heterogeneous composites, PLCs promise a material exhibiting the low cost of heterogeneous engineering as well as the exemplary mechanical and other physical properties of PLCs.

Here we explore the possibility of combined reinforcement on a macroscopic and molecular scale. The influence of the differences in reinforcement provided by glass and PLCs is evaluated. Two-ply composites of cowoven fabric are used as the control sample. Interlayers manufactured by extruding PP + PLC blends in varying PLC concentrations are introduced into the composite. The interlayers consist of an extruded polypropylene (PP) matrix and PET/0.6PHB PLC (where PET = poly-(ethylene terephthalate), PHB = *p*-hydroxybenzoate, and 0.6 = the mole fraction of PHB in the PLC). Dynamic mechanical analysis is used to determine the influence of the PLC on the glassy plateau modulus (storage modulus - temperature profiles) and change in damping capability (loss modulus - temperature profiles). The influence of these interlayers on the interfacial properties of the composites is studied through the influence on crystallization kinetics. As Moon (9) states for semicrystalline thermoplastic matrices, interfacial morphological features arise along the interface owing to indirect influence of the fibers on the crystallization process. There have been many reports of "transcrystallinity" or development of columnar crystallites in the direction of the fibers (10-13). The influence of blending in the matrix has also been studied. Amash *et al.* (14) report on the influence of short glass fibers on blends of PP and PP/ethylene propylene copolymer. The short fibers increased the crystallization temperature of PP but did not change the percent crystallinity.

The extruded interlayers are studied to evaluate the influence of the glass fibers. The potential benefits of replacing a heterogeneous ply with a molecular composite are evaluated by comparing a one-, two-, and three-ply composite to a two ply composite containing an interlayer.

Table 1. Nomenclature.

Configuration	Description	Nomenclature
PP + GF cowoven mat	1 Ply	1L
	2 Ply	2L
	3 Ply	3L
PP + PLC Interlayer	0% PLC	000B
	15% PLC	015B
	25% PLC	025B
	35% PLC	035B
	50% PLC	050B
	100% PLC	0100B
Two ply PP + GF cowoven mat and PP + PLC interlayer	Interlayer of 0% PLC	000C
	Interlayer of 15% PLC	015C
	Interlayer of 25% PLC	025C
	Interlayer of 35% PLC	035C
	Interlayer of 50% PLC	050C
	Interlayer of 100% PLC	100C

2. EXPERIMENTAL

2.1. Materials

- Polypropylene (13T10A) supplied by Rexene Corp.
- PET/0.6PHB Polymer Liquid Crystal (LC-3000) supplied by Unitika Corp., Kyoto, Japan.
- Twintex Polypropylene/Glass-Fiber Woven Cloth (TPP6024CNO) supplied by Vetrotex Certaineed, Wichita Falls, Tex. (volume fraction of glass: 35%).

2.2. Nomenclature

The PP + PLC interlayers contained 0, 15, 25, 35 and 100% by weight of PLC. To promote clarity in regard to the large number of samples, the samples have been labeled systematically. Table 1 provides the nomenclature of samples and their characteristics. Note that the single-layer samples of PP and PLC will be designated by the PLC wt% followed by B, signifying a blend. The glass-fiber + PLC composite set will be designated similarly, but followed by a C, designating a composite. Also note that the control samples of cowoven PP + glass mat having one, two, and three plies will be referred to as 1L, 2L, and 3L, respectively.

2.3. Sample Preparation

2.3.1. Interlayers

Interlayers were extruded and studied as-is as well as between two-ply composites. The control samples were composites consisting of the cowoven mats with no interlayer. Preparation of samples containing PLC consisted of compounding the PP and PLC pellets using a 0.5 inch Randcastle laboratory extruder (Microtruder) operating at approximately 35 rpm with averages of 220°C zone temperature and 200°C die temperature. Blends of the six different PP + PLC compositions were extruded as 0.5-cm-wide tape using a custom-fabricated tape die. The extrudate had good directional alignment from shear within the extruder, producing parallel PLC fibers embedded in a PP matrix. Samples were compressed between DuPont Kapton polyimide film-covered compression plates in a DAKE compression-molder (model #44-250) at 165°C under pressure of approximately 0.9 metric ton per 13 cm-diameter ram. The compression cycle involved heat-up of the compression molder to molding temperature, 15-min sample heating phase, 10-min compression phase, and water-cooling to 40°C. DMTA sample coupons were cut from the resultant film, noting directional alignment of PLC fibers.

2.3.2. Composite

Bi-directional Twintex PP/GF mats were compression molded at 180°C under constant pressure of 1.3 metric tons per 13 cm diameter ram using the heat-cool cycle indicated above. For composites containing the interlayer, the PLC fiber direction was noted during processing.

2.4. Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical tests were carried out on a Polymer Laboratories DMTA in dual cantilever bending mode configuration. Single-frequency tests at 1 Hz were performed on all samples from -50°C to 150°C at strain level 4 (nominal peak to peak displacement of 64 microns). The heating rate was $3^{\circ}\text{C}/\text{min}$. Values of the loss factor ($\tan \delta$), storage modulus (E'), loss modulus (E''), and complex modulus (E^*) were obtained.

2.5. Differential Scanning Calorimetry (DSC)

Sample coupons were heated at $10^{\circ}\text{C}/\text{min}$ to 180°C and annealed for 20 min. Annealing removed frozen-in stresses and defects, allowing for accurate readings describing both crystallization and thermal properties. The samples were then quenched to 30°C . This was followed by a slow heat and cool at $10^{\circ}\text{C}/\text{min}$ between 30°C and 180°C . Specific heat curves were calculated and the peak temperature, peak area, and onset temperatures were noted.

2.6. Thermogravimetric Analysis (TGA)

Thermogravimetric (TGA) tests were conducted on all samples using a Perkin-Elmer 7 Series thermo-

gravimetric analyzer (TGA-7). Samples were heated from room temperature to 900°C to separate the glass fibers and matrix by vaporization of the PP and PLC matrix. From this data, glass volume fractions and weights were obtained by comparing the original composite weight to its glass weight.

3. RESULTS AND DISCUSSION

3.1. Dynamic Mechanical Analysis

The dynamic mechanical test results of the composites with an interlayer are shown in Fig. 1. The plateau modulus increases at low PLC concentrations and then drops substantially. In contrast to the blends, the terminal region is delayed to higher temperatures because of the glass reinforcement holding the matrix together. The matrix absorbs the shocks that the brittle fibers of the composite cannot withstand and holds the fibers in place. The glass transition temperatures of the polypropylene is $\cong 0^{\circ}\text{C}$ while that of the PLC copolymer, as we have earlier reported, is 60°C for the PET fraction and 150°C for the PHB fraction (8). From the loss modulus (E'') curves, it is apparent that the transition of neither PLC component is discernable. The single peak around 6°C corresponds to the PP

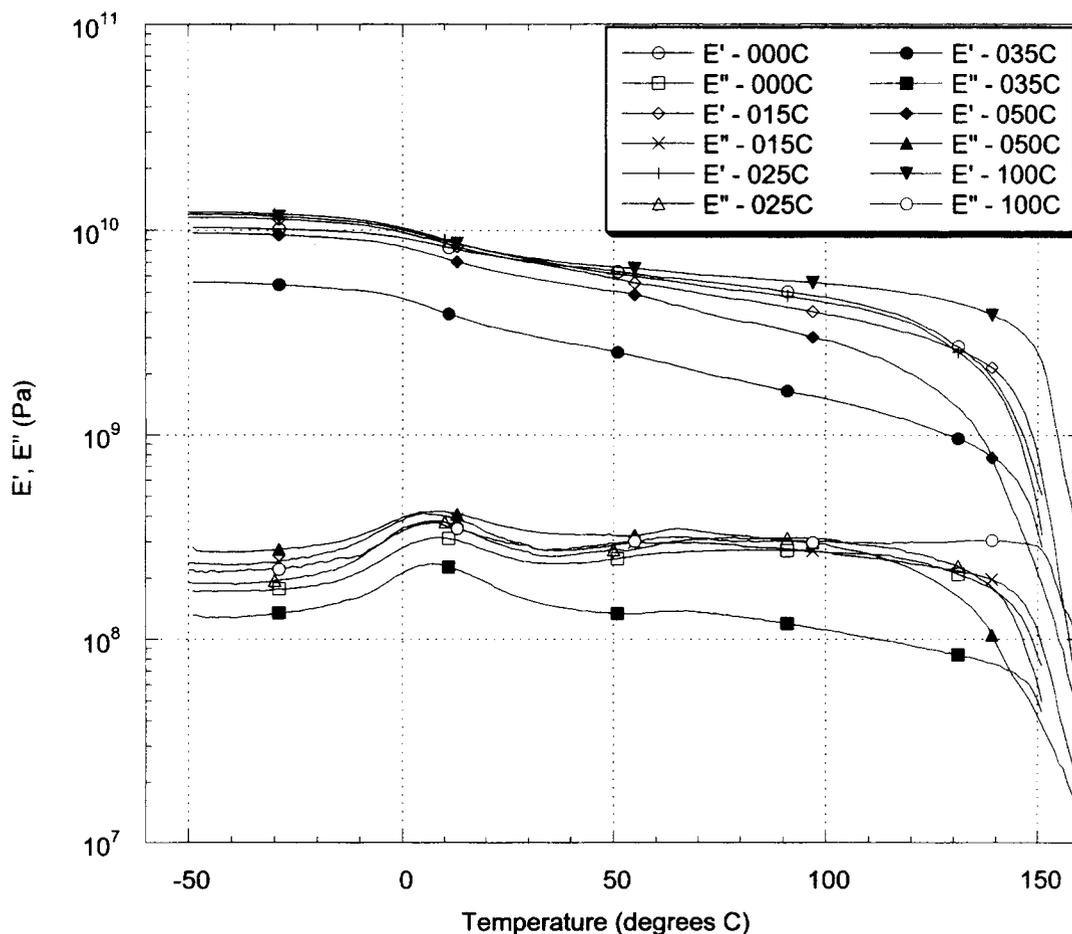


Fig. 1. Storage and loss moduli of the composites with an interlayer.

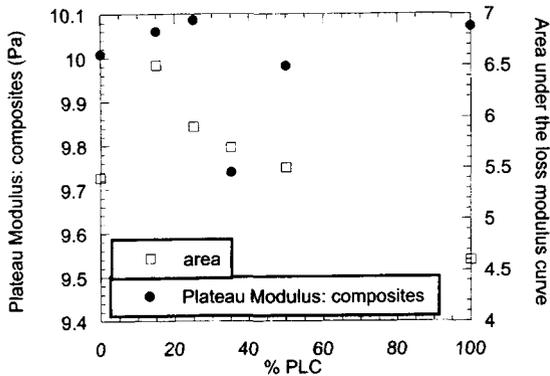


Fig. 2. Plateau moduli and area under the loss modulus of composites containing an interlayer.

component. There is no shift in the transition peak temperature with increasing PLC content. This indicates that the PLC does not affect the amorphous moiety of the PP. The absence of thermodynamic miscibility is no barrier to mechanical compatibility as has been shown for systems containing poly(vinyl chloride) (15, 16).

The plateau modulus, however, is affected by the PLC components. As shown in Fig. 2, the values show an increase at low concentrations of PLCs with a strong negative deviation with regard to the constituents at mid compositions. We draw on earlier results concerning the role phase transitions play in systems containing PLCs as a constituent (17). From the phase diagram of PET/ θ PHB copolymers as a function of θ , it has been found that around $\theta = 0.2$ we reach the θ_{LC} limit at which islands of the LC rich phase are formed. This is analogous to phase separation/coalescence behavior seen in polymer blends. The islands have been observed by scanning electron microscopy (SEM) in PET + PET/0.6PHB blends (18). A further study of the islands by wide angle X-ray scattering (WAXS) shows that the islands with sizes 1.0 to 1.4 μm contain in turn crystallites with an average diameter of ≈ 12 nm (19). The degree of exclusion of the flexible constituent (PET) is higher inside the crystallites than in the islands, but the connectedness produces increasing PHB concentrations also in the matrix along with increasing overall PLC contents. This occurs until saturation of the LC-poor matrix with the LC-rich phase.

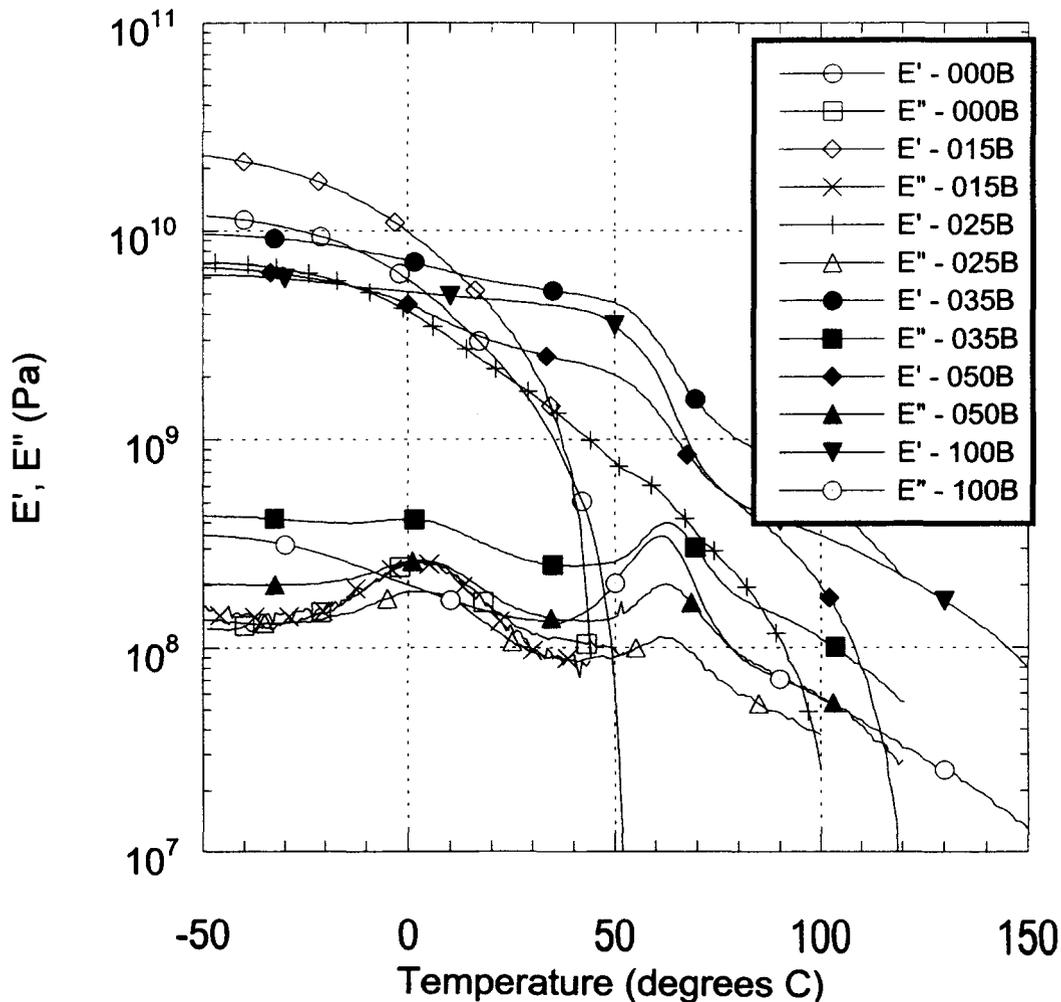


Fig. 3. Storage and loss moduli of the interlayers.

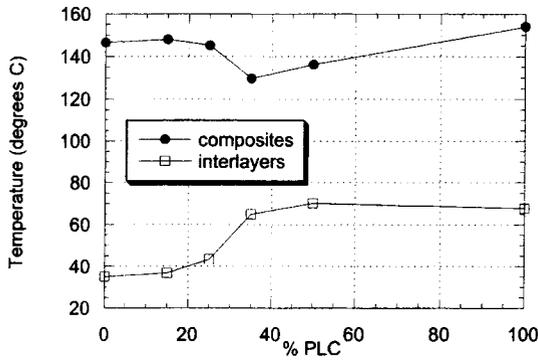


Fig. 4. Temperature corresponding to the storage modulus of 1 GPa.

Similarly, we observe a PLC concentration effect on the interlayer in the composites. At low concentrations of the PLC phase, the newly formed islands only disrupt the structure of the PP matrix (because of limited solubility of the PLC in PP). Hence the significant lowering of the E' for the 035C composite. Further addition of the PLC to the interlayers raises E' ; see the curve for 050C. The connectedness of the PET and PHB sequences in the PLC plays a role here too, and the PHB sequences provide reinforcing capability. For the pure PLC interlayer composite (100C) we have at elevated temperatures (starting from 55°C or so) the highest E' values of all compositions.

As pointed out by Ferry (20), toughness or dissipated energy due to small scale oscillations is related to

the area under the loss component of dynamic modulus-temperature plot. As the ordinate on the right-hand side of Fig. 2 shows, all samples have larger areas than their individual components (00C and 100C). Moreover, we see that the samples 15C and 25C show the highest values, once again affirming the observation of better improvement in low PLC percentages.

The suppression of the glass transition of either PLC component (60°C and 150°C for PET/0.6PHB (8)) is due to the presence of the glass fibers. Thus the DMA of the extruded interlayers show both transitions in the loss modulus-temperature profiles (Fig. 3). As can be seen, the polypropylene has a high plateau modulus, but it drops rapidly with increasing temperature. There is no discernable rubbery plateau. From the storage modulus curves we can see that the initial modulus increases upon addition of the PLC to the pure PP interlayer; a sharp drop upon formation of the island phase; and a gradual increase afterwards when the rigid PHB constituent manifests itself both in the islands and in the matrix.

The introduction of the PLC provides increased dimensional stability for longer temperatures—as evidenced by the shoulder corresponding to the PLC transition shifting to the right. Glass transition temperature (T_g) peaks occur when the constituent polymers undergo a distinct phase change from glassy to amorphous (21, 22). The most conspicuous T_g peak occurs in all samples at 10°C, and can be attributed to polypropylene's glass transition temperature. All PLC-containing samples displayed similar trends.

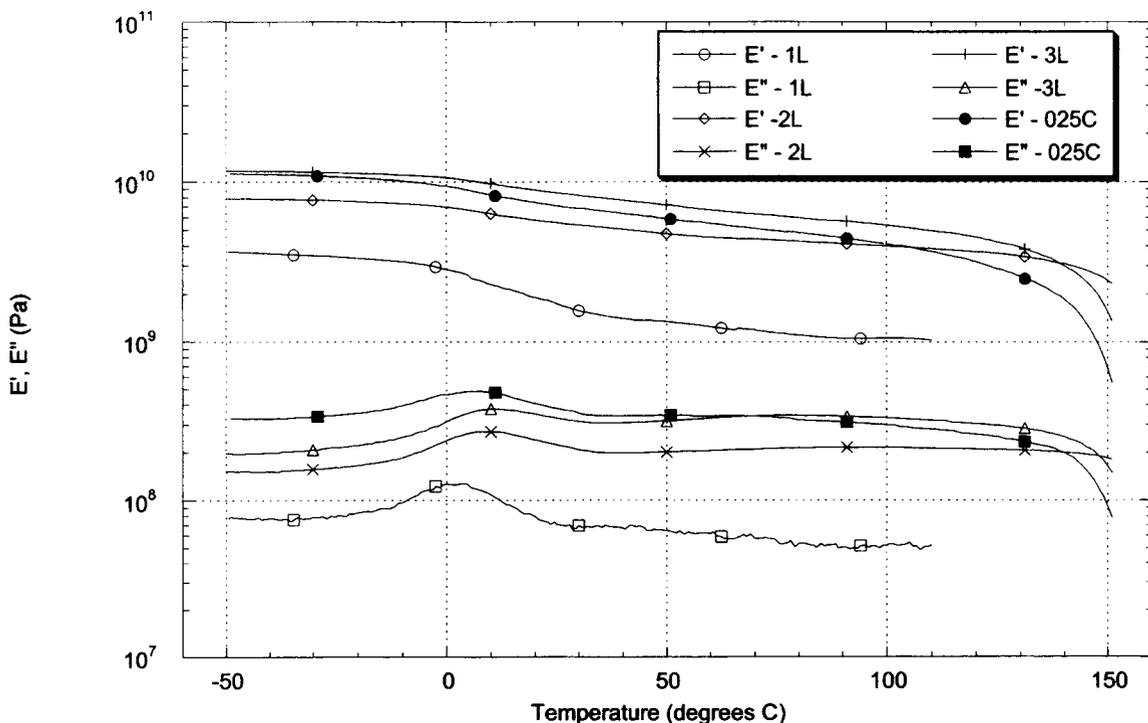


Fig. 5. Storage and loss moduli of one-, two-, and three-ply composites and a two ply composite with a 25% PLC interlayer.

Fig. 6a. Melting endotherms of the as-processed interlayers and composites.

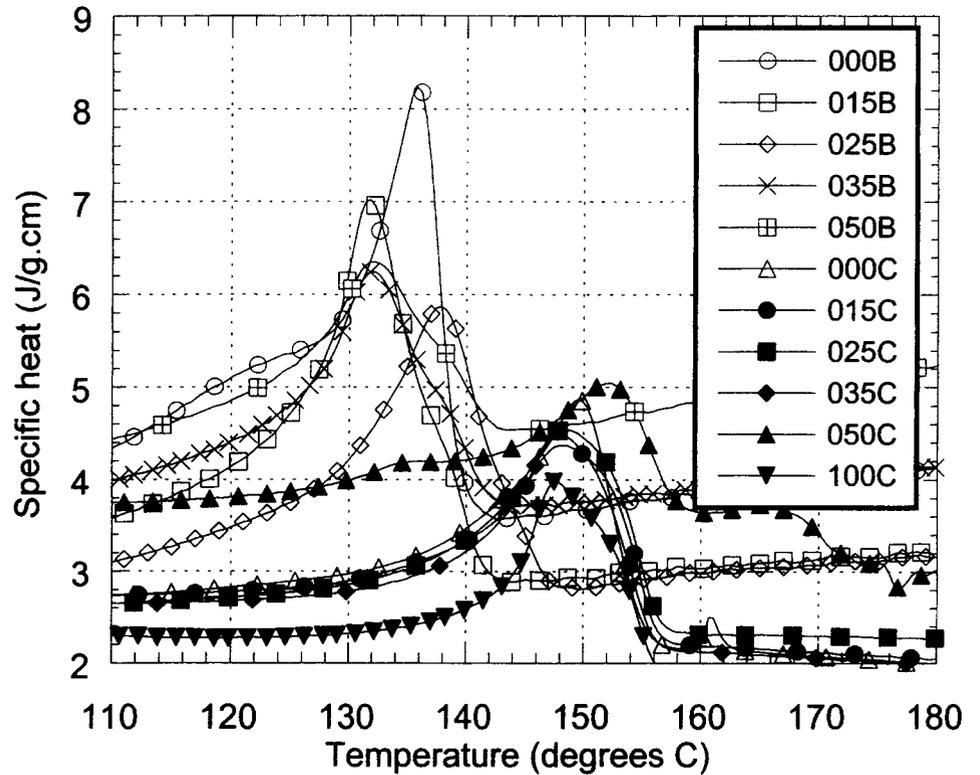
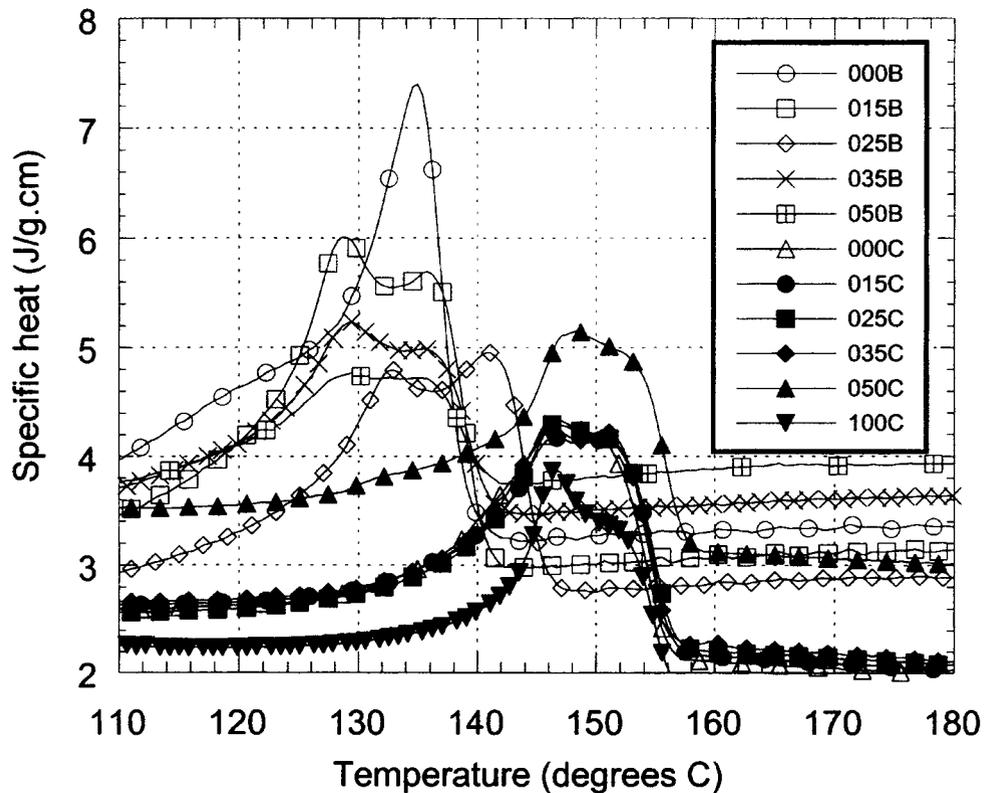


Fig. 6b. Melting endotherms following quench from melt.



Again, there is no shift in the values of the peak temperatures, indicating a lack of thermodynamic miscibility between the components. Apparently the flexible

PP interlayer also contributes to the mechanical integrity of the composite, providing additional protection for the brittle glass fibers. We note in this context

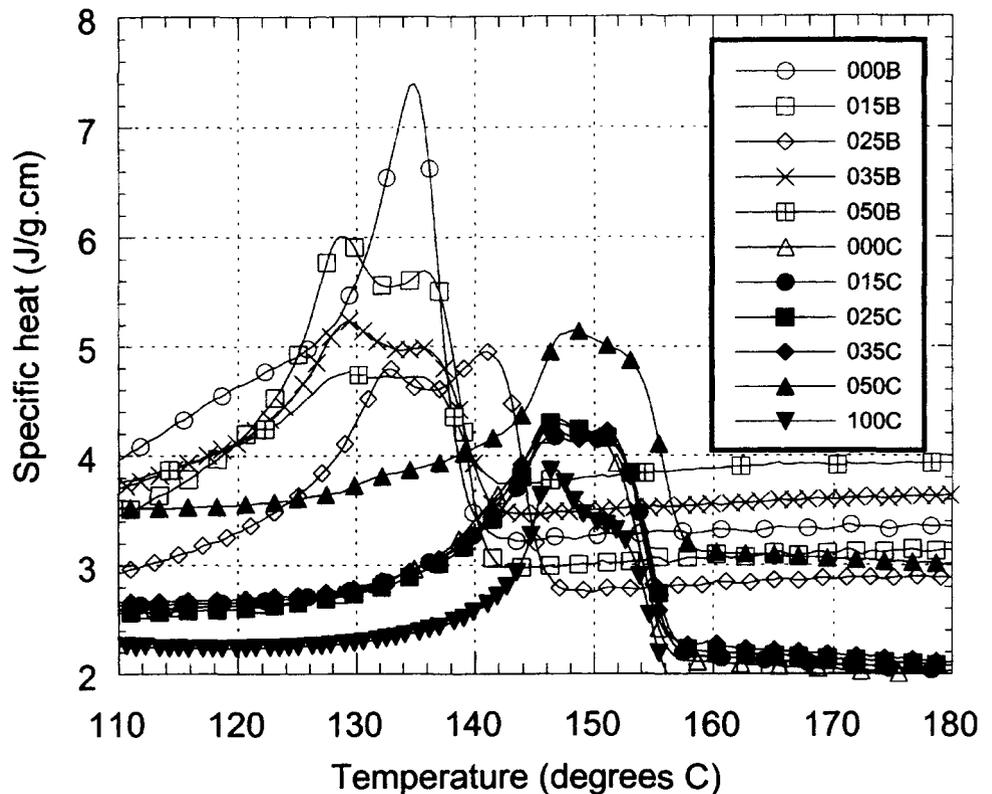


Fig. 6c. Crystallization during slow cooling.

the results of Osten *et al.* (23), who have compression molded Twintex with randomly oriented chopped glass fibers. They obtained car bumpers with impact strength increased by 130% over the unmodified cowoven composite.

As mentioned earlier, PP gains dimensional stability from reinforcement with glass fiber. Temperature values corresponding to the modulus of 10^9 Pa from Figs. 1 and 3 are shown in Fig. 4. As can be seen, the interlayers themselves are affected by the presence of the PLC with a shift to higher temperatures with increasing PLC content. The shift to higher temperatures due to purely molecular reinforcement is limited to 64°C (that is, up to the glass transition temperature of the PET). In contrast, heterogeneous composites of the PP + glass now retain dimensional stability to 150°C or so. Introduction of the interlayers retains dimensional stability for low PLC concentrations but higher loadings decrease the related temperature. Combining these results with the toughness calculations (Fig. 2), we can infer that an increase in dimensional stability with simultaneous increase in toughness is obtained for composites containing low loadings of PLC.

It is important to realize that in comparing the macroscopic reinforcement (glass fibers) to the molecular reinforcement (PLCs) we have synergistically obtained the benefits of the higher modulus of the former with the lower specific weight of the latter. Figure 5 shows the influence of increasing the number of plies

of the cowoven mat. As the number of layers increases, the modulus of the material are expected to increase owing to increased fiber content, and that is the case here (Fig. 1). Comparing each sample, we can see that the single-layer sample 1L is considerably softer than the other samples 2L and 3L. As the number of layers increases, the modulus increases dramatically. Recall that these values are on a logarithmic scale, so the difference in log modulus between single-layer and triple-layer composites by an integer represents a tenfold difference in the stiffness. As can be seen, the two-ply composite with a PLC interlayer has comparable modulus values to the three ply cowoven PP + glass composite. This is accompanied by substantial weight savings owing to the necessarily lower fraction of glass in the two layer composite over the three layer one.

3.2. Thermal Analysis

The DSC results of the as-processed samples, post annealed, and slow cooled interlayers and composites are shown in Figs. 6a, 6b, and 6c, respectively. In the as-processed state, the melting point of the composites is increased with respect to the interlayers. This is due to the thermal lag associated with the presence of glass fibers in the sample coupon. The increased height of the interlayer peaks in comparison to the composite peaks indicate a decreased crystallinity due to glass fiber presence. After quenching the samples, the second heating curves shows distinctive behavior

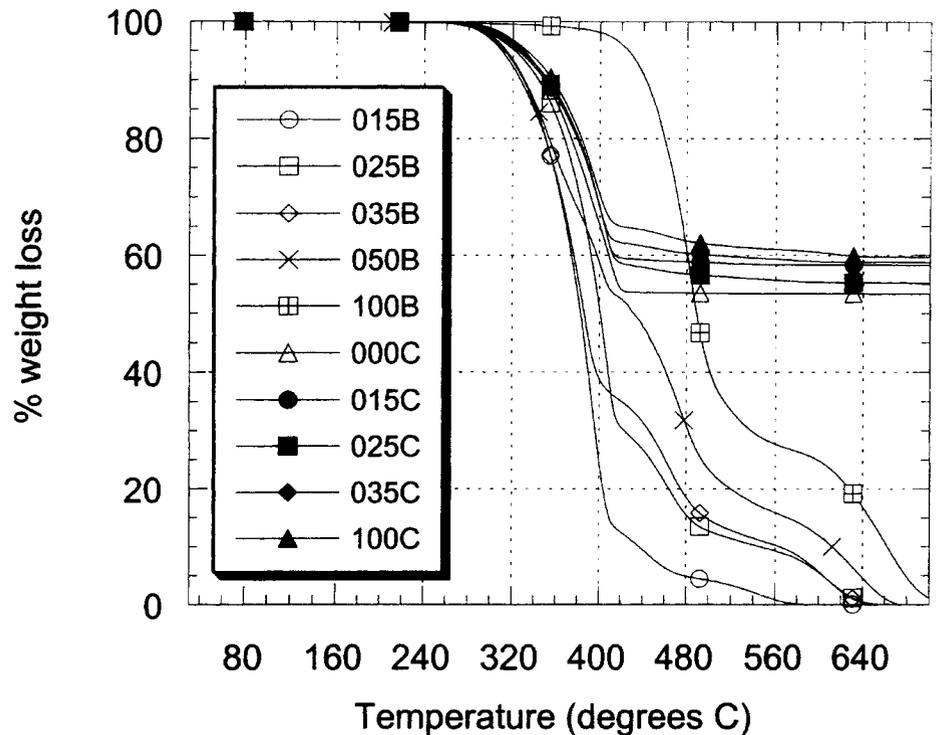


Fig. 7. Thermogravimetric analysis of interlayers and composites.

with respect to the first heating ramp. Comparing the results, it can be seen that there is no marked change in melting temperatures. However, for all samples containing PLCs, a melting point peak doublet is present. This indicates that the PLC acts as a secondary nucleating agent in the blend, resulting in two distinct crystalline morphologies. It is relevant to note that even in samples containing 100% PLC, the melting peak is reflective of the PP present in the glass + PP cowoven mat. The crystallization behavior during the slow cooling stage following the slow heating stage shows the influence of the PLC fraction. The crystallization temperatures of the glass reinforced composites are higher than those of the pure interlayers. This is due to the nucleating effects of glass. The PLC component also serves as a nucleating agent. Comparing the peak temperatures of the pure PP interlayer (00C) to those of the PP + PLC interlayer composites, it can be seen that for small loadings the largest drop in crystallization temperatures occurs. The samples having a pure PP interlayer have no marked change in crystallization temperatures compared with their composite. The effects of the presence of other blend constituents on the crystallization of a given constituent were noted by Grebowicz and Pakula (24) for flexible polymer blends and by Brostow *et al.* for PLC containing constituents (18). The rigid units in a PLC provide alignment for other constituents (25).

The influence of temperature on the degradation kinetics is markedly different for the composites in com-

a single kinetic rate. Complete degradation of matrix occurs at 420°C. In contrast, the interlayers have multiple degradation steps with complete degradation occurring only at 680°C. This indicates that an interphase due to the glass fiber sizing and the matrix serves to accelerate degradation once initiated.

4. CONCLUDING REMARKS

Engineering polymers such as PP can be reinforced at the macroscopic level with a variety of higher modulus materials such as fibers, beads, and cement, thus forming heterogeneous composites (18). Thus, reinforcing polypropylene with glass fibers as a cowoven mat has many advantages. Alternatively, reinforcement can also take place at the molecular level. Here we have examined the benefits of simultaneous molecular and macroscopic reinforcement. Low fractions of PLCs serve to increase the damping energy as well as increase the glassy plateau modulus. Long term dimensional stability is mainly influenced by the presence of the woven glass fiber fraction in the cowoven mat. However, higher loadings of PLC have detrimental effects on the dimensional stability, causing interply slip at lower temperatures. Benefits to using a PLC ply between the cowoven mat are mainly associated with the weight savings to be gained by using a material with lower specific gravity. There might be other potential advantages of PLC use, given the unusual properties of these materials (26, 27).

parison to the interlayers—as the TGA results in Fig. 7 indicate. The single slope associated with the composites indicates that the degradation mechanism has

The crystallization kinetics of the composites are affected by the nucleating effects of the PLC and the glass fiber. When both components are present, the

glass fibers dominate the nucleation kinetics. This is also reflected in the degradation kinetics, where complete degradation of the matrix occurs at lower temperatures for the glass reinforced materials.

ACKNOWLEDGMENTS

Financial support has been provided by the State of Texas Advanced Technology Program (Project #003661-047). We are also grateful for the material and technical support provided to us by Messrs. Fred Krautz and Sam Osten of Vetrotex Certainteed, Wichita Falls, Tex., as well as to Perkin-Elmer Corp. for their equipment donation. Useful discussions with Prof. Roy Arrowood, University of Texas at El Paso, and Prof. József Karger-Kocsis, University of Kaiserslautern, Germany, are also acknowledged. Two of us (C. S. O. and D. S.), acknowledge the Texas Academy of Mathematics and Sciences, University of North Texas, for their support in the high school research-university collaborative programs.

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