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Crystallization behavior of polypropylene and its effect on woodfiber composite properties

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Abstract

This paper describes an approach where polarizing optical microscopy is used to observe the crystallization process of different polypropylenes in the presence of woodfiber. The crystallization behavior was found to be related to the chemical composition of the polymer systems and the addition of maleic anhydride grafted polypropylene (MAPP) to polypropylene dramatically altered the crystal structure around the fiber, even at low levels (1 to 2%). For neat polypropylene, the woodfiber showed poor nucleating ability, and little difference in bulk and surface crystallization was observed. However, when MAPP was added (1 to 10%), the nucleation density at the woodfiber surface became so pronounced that a transcrystalline layer was formed around the fiber. Because the woodfibers themselves had not undergone any prior chemical modification, the increase in nucleation ability of the fiber surface must be attributed to specific interactions between the woodfibers and the maleic anhydride moiety of the MAPP. These observations reveal that the MAPP may not only interact with woodfibers, but may also change the microstructure of the matrix near the fibers. It was observed that the nucleation of the woodfiber surface was selective, indicating that the local physical or chemical characteristics of the fibers might have some influence on the polypropylene crystallization. Dynamic mechanical analysis was used to monitor isothermal crystallization of the polypropylene blends, and provided some additional insight into the contribution of crystalline morphology to strength properties.

Introduction

As a semicrystalline polymer, polypropylene easily crystallizes as spherulites when the crystal-

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lization proceeds from the melt. The nuclei originating spherulitic growth are generally believed to be foreign bodies in the bulk (e.g., catalyst residues, antioxidants, fillers, or specific nucleating agents). In the presence of certain fibers, preferential crystallization can occur if the fiber surface can nucleate crystalline growth. Isolated spherulites may start to grow at various points along a fiber. However, if the nucleation density is sufficiently high, the embryonic spherulites begin to impinge on each other, so that the normal three-dimensional growth is impossible and consequently the spherulites grow predominantly in one direction, normal to the surface (2). The development of such a crystalline layer is termed transcrystallization and the layer of surface nucleated material is referred to as the transcrystalline layer.

The effect of transcrystallization on the mechanical properties of the interface and/or the overall composite properties is highly fiber/matrix specific (1,2). Several researchers have reported or suggested that the polypropylene transcrystallization around cellulose or woodfiber could improve the interfacial adhesion in the composites (1–4,5,6). Gray (3) found that bleached woodfibers had a nucleation ability similar to that of cotton fibers, giving a cylindrical transcrystallization region of about 0.1 mm in diameter along the entire length of each fiber. However, for high-yield wood pulps (unbleached softwood kraft and sulfite fibers), the presence of lignin, hemicellulose, or possible surface contaminants prevented the formation of such a layer. Felix and Gatenholm (1) showed that a transcrystalline layer could develop around purified cotton fibers, and it improved the interfacial shear transfer and the tensile strength of the composite. Wang and Harrison (6) observed, using optical microscopy, that silane-coated woodfibers nucleated more spherulites than untreated fibers. These previous studies have demonstrated the potential nucleation ability of woodfibers to induce the transcrystallinity of polypropylene.

Although the surface modification of woodfibers is a common approach to improve the interfacial adhesion, other alternatives may have more potential in commercial production, such as adding a coupling agent or compatibilizer in the manufacturing process or changing the composition of the polymer. When a compatibilizer is added to the wood-polymer system, the nature of the fibers may be modified due to the interaction between the fiber and the compatibilizer, and consequently the nucleation ability of the fibers may be changed. The aim of this preliminary study was to investigate the crystallization behavior of polypropylene, maleic anhydride grafted polypropylene (MAPP), and blends of the two polymers. Also studied was the evolution of the mechanical property of model wood-plastic composites, which could provide some information to help establish critical process parameters.

Experimental

Materials

The polypropylene and MAPP were commercial products, EXXON PP-7292W and Epolene G-3003, respectively. The polymer blends containing different mass fractions (1, 2, 5, and 10%) of MAPP were compounded with a Brabender single-screw extruder at 210°C. Two wood species, maple and aspen, were used in the experiments.

Methods and equipment

Polarizing optical microscopy was used to observe the crystallization of the polymers in the presence of woodfibers. The microscope was a Zeiss Universal equipped with a Leitze 350 Heating Stage, and a Nikon F2 Camera for recording crystallization. Dynamic mechanical analysis (DMA) was conducted using a Rheometrics RSA-II Solids Analyzer. A Perkin-Elmer Model DSC-7 differential scanning calorimeter was used for thermal analysis of the polypropylene blends.

Sample preparation

Two types of samples were used in the microscopic observation: single fiber and multi-fiber (maple). The single fiber (about 0.13 to 0.15 mm thick, 0.20 to 0.40 mm wide) was cut from a microtomed slice and placed between two plastic films. The sample was heated at 200°C for 10 minutes to melt the films and then transferred quickly to the microscope heating stage. For the multiple-fiber samples, six slices were laminated with plastic films. The sample was cut with a microtome perpendicular to the laminate surface and melted at 200°C for 10 minutes before transferring to the microscope heating stage. The dimensions of the fibers were approximately 0.15 by 0.15 mm.

The DMA samples were model composite laminates composed of two maple or aspen strands (0.6 to 0.7 mm thick) adhered by melting a plastic film at 200°C for 15 minutes under slight pressure. The dimensions of the samples were approximately 1.4 by 6 by 50 mm.

Measurement conditions

The microscopic observation was carried out at 135±1°C either by direct observation through the eyepieces or by photographically recording the crystallization process. The model composite sample was excited using a dual cantilever fixture to follow the evolution of the mechanical property. When the DMA measurement was made, the temperature was first raised to 200°C for 10 minutes to melt the plastic. Then the temperature was decreased to 135°C to induce crystallization. The strain amplitude applied was 5 x 10^{-4} and the excitation frequency was 1 Hz.

Results and discussion

Crystallization behavior of the polymers

Polarizing optical microscopy is routinely utilized to study the crystallization process of polymers as it provides direct information on the nucleation and crystal growth. Figures 1 to 3 show, respectively, the micrographs of the polypropylene, MAPP, and a polypropylene-MAPP polymer blend (2% MAPP) crystallizing from melt at 135°C for 10, 15, and 20 minutes in the presence of a single woodfiber. These figures demonstrate the different crystallization behaviors of the neat polypropylene compared with the MAPP and the polypropylene-MAPP blend. The nucleation density of the MAPP and the polymer blend at the woodfiber surface was much higher than that of the polypropylene for at the same time.

When the polypropylene melt containing a single fiber was placed on the heating stage at 135°C, some nucleation sites appeared and became observable on the micrograph after about 10 minutes, both on the fiber surface and surrounding the fiber (Fig. 1). The nucleation density at the fiber surface was similar to the bulk phase and the nucleation sites at the fiber surface were apart from one another. Although surface crystallization was noted, the relatively poor nucleation ability did not result in a continuous transcrystal-

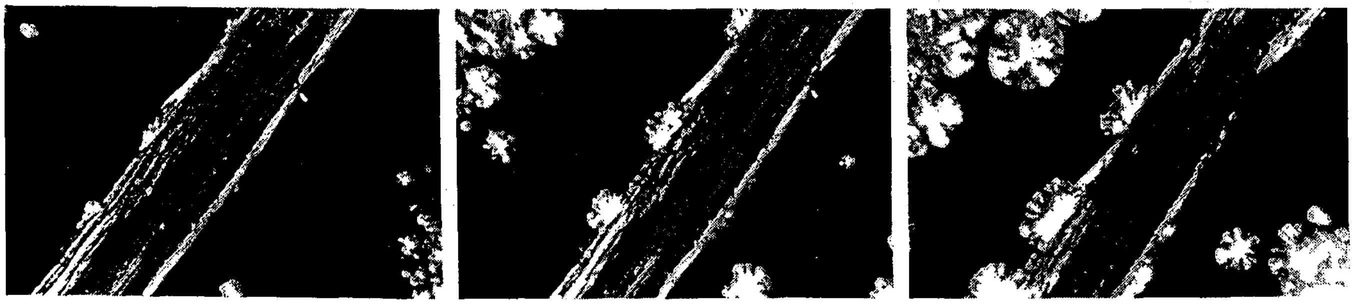

Figure 1. ~ Optical *micrographs* (actual dimensions 1.5 by 1 .O mm) of polypropylene melt *crystallizing* at 135°C *in* the presence of *single woodfiber* for *(left) 10 minutes;* (middle) 15 minutes; and (right) 20 minutes.

Figure 2. ~ Optical micrographs (actual dimensions 1.5 *by 1.0 mm) of MAPP* melt *crystallizing* at 135°C in the Presence *of* single *woodfiber for (left)* 10 minutes; (middle) *15 minutes; and (right) 20 minutes.*

line layer around the fiber. These observations are in agreement with those obtained earlier by other researchers for high yield wood pulps (3), untreated woodfibers (6), and bamboo fibers (4).

It was also noted that the nucleation of polypropylene onto the woodfiber surface was selective. The nucleation sites were more likely to appear at the regions where fibrils protruded from the surface. This indicates that the local chemical and/or topographical nature of the fiber plays an important role in the nucleation process for polypropylene.

The MAPP showed a quite different crystallization behavior compared to the polypropylene. When cooled from the melt, many nucleation sites appeared at the fiber surface after about 5 minutes, while the nucleation density in the bulk was noticeably lower. The nucleation density at the fiber surface was so extensive that the embryonic spherulites impinged on each other and a transcrystalline layer became apparent at 10 minutes. Figure 2 demonstrates that the crystallization of MAPP in the presence of woodfibers was surface dominant. The formation of a transcrystalline layer in the case of MAPP may be an indication of an improved interfacial adhesion between the woodfiber and the m&ix, which resulted from the interaction between the hydroxyl groups of the fiber surface and the grafted maleic anhydride moiety of the MAPP (4).

It is interesting to note that the crystallization behavior of the polymer blend was closer to MAPP than to polypropylene, although its main component was polypropylene (Fig. 3). The nucleation density on the woodfiber surface was remarkably higher than in the bulk phase, and a transcrystalline layer could develop around the fiber. Comparing Figures 1 and 3, it was clear that the polypropylene crystallization process was altered dramatically by the addition of MAPP, even at low levels (1 to 2%). The difference in crystallization between the polymer blend and MAPP resided mainly in the rate of the nucleation. The appearance of nuclei. (induction time) seemed to

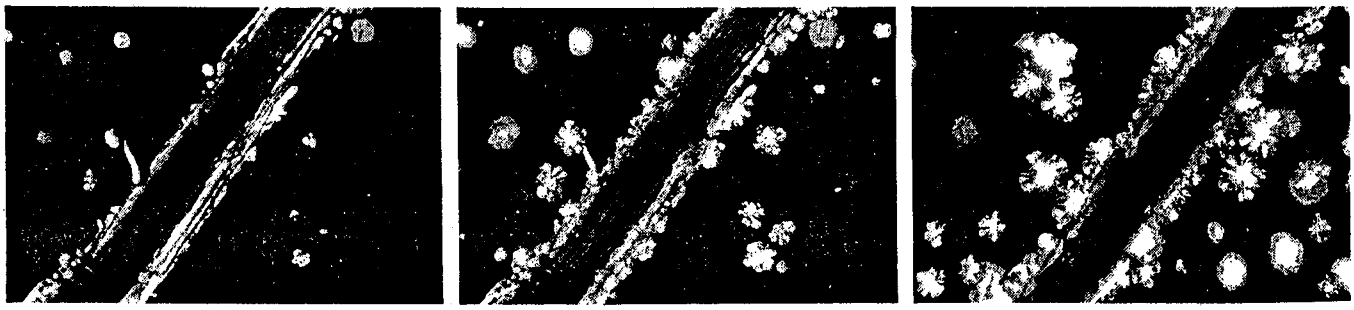

Figure 3. ~ *Optical* micrographs (actual dimensions 1.5 by 1 .O *mm) of* polypropylene-MAPP (2%) polymer blend *melt* crystallizing at 135°C in the presence of single *woodfiberfor* (left) 10 minutes; (middle) 15 minutes; and (right) 20 minutes.

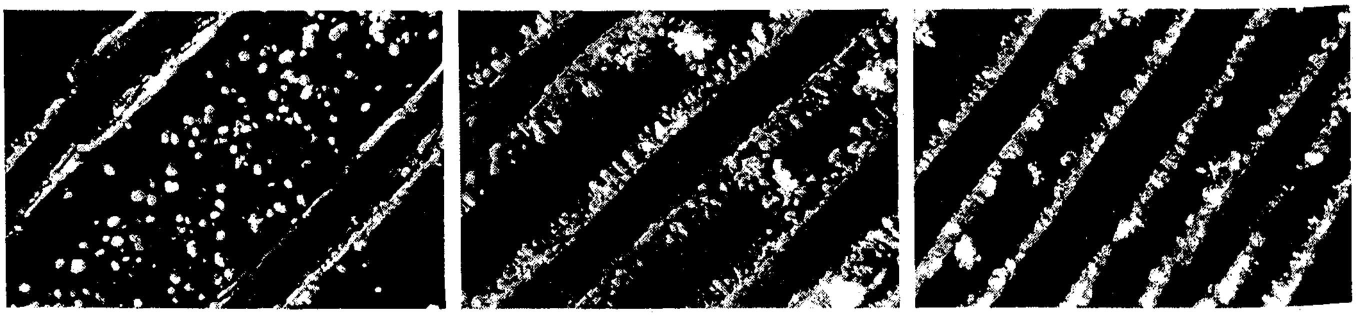

Figure 4. ~ Optical *micrographs (actual* dimensions 1.5 by 1 .O mm) of (left) polypropylene; (middle) MAPP; and (right) polypropylene-MAPP (10%) polymer blend melts crystallizing at 135°C for 15 minutes in the multi-fiber samples.

take longer, and the thickness of the transcrystalline layer was less in the polymer blend system than in MAPP at similar times. Because the wood-fibers had not undergone any prior chemical modification and the matrix was mainly composed of polypropylene, the increase in nucleating ability of the fiber surface for the polymer blend must be attributed to the interactions between the wood-fibers and the maleic anhydride moiety in the polymer blend. The formation of the transcrystalline layer reflected the consequence of these interactions, resulting in higher nucleation ability for polypropylene. The relative lower rate of nucleation for the polypropylene blend, compared to the case of MAPP, may infer that the maleic anhydride moiety migrated from the bulk to the fiber surface and a certain time was required for this migration to occur.

The different crystallization behavior of the polypropylene compared to the MAPP and the polypropylene-MAPP blend can be seen more clearly in the multi-fiber samples (Fig. 4). At 15 minutes, spherulites were located essentially in the bulk and few crystals appeared on the fiber surfaces in the polypropylene sample. In the MAPP and polypropylene-MAPP blend samples, the nucleation sites were concentrated at the fiber surface and a transcrystalline layer around the fibers could be readily identified.

Differential scanning calorimetry was used to further study the crystallization process of the filled (30% aspen flour) and unfilled polymers. The results are summarized in Table 1. The addition of small amounts of MAPP to polypropylene slightly reduced the temperature (T_c) and extent of crystallization (ΔH_c). When wood flour was added to the polymer systems, the crystallization temperature increased slightly while the heat of crystallization was not significantly affected. This suggests that crystallization behavior may arise from the relative position of the experimental, isothermal temperature (T_i) to the polymer's crystallization temperature. That is, the T_c of the bulk MAPP-containing polymers is 5” to 8°C lower than the corresponding wood-filled composites. By virtue of this difference, bulk crystallization would be expected to proceed at a slower rate. This further illustrates the significance of wood-polymer interfacial interaction on crystallization characteristics and composite performance.

Evolution of the storage modulus of model composites

DMA measures the viscoelastic properties of polymeric materials and composites. The storage modulus (E’), loss modulus (E”) and the loss factor (tan 6) of the material can be readily obtained with the appropriate testing configuration. In this study, changes in E” and tan δ were too small to extract useful information. Consequently, only E’ and its first time derivative (dE'/dt) were used to characterize the effect of polymer crystallization on the evolution of mechanical properties.

Figure 5 shows the evolution of the storage modulus of maple, maple-MAPP, and maple-polypropylene composites with time at 135°C. The evolution of the storage modulus of a polymer blend composite is shown in Figure 6. The initial temperature was 200°C and it was decreased to 135°C within 2 minutes. The sample's temperature achieved equilibrium in 3 to 4 minutes, and the measurement started when the temperature of the DMA oven began the decrease from 200°C.

The modulus of maple did not change with time, while that of the composites increased with

Table 1. ~ Variation in crystallization behavior of *unfilled* and *filled* (30% *aspen flour)* polypropylene-MAPP blends determined by *differential* scanning *calorimetry.*

Blend composition	Unfilled polymer		Filled polymer	
	T_c	ΔH_c	T_c	ΔH_c
	(°C)	($J \cdot g^{-1}$)	(°C)	($J \cdot g^{-1}$)
100% polypropylene	115.1	-108.3	113.6	-86.1
2% MAPP + 98% polypropylene	111.0	-83.6	116.9	-86.0
5% MAPP + 95% polypropylene	111.6	-84.9	116.1	-84.2
10% MAPP + 90% polypropylene	111.3	-84.8	119.5	-86.9
MAPP	112.9	-91.6	119.3	-93.8

time (Fig. 5). This increase could only be attributed to the solidification of polymer with crystallization, as the modulus of wood itself kept constant. Consequently, the rate of the modulus increase reflected the crystallization rate of the polymer phase and could be used to characterize the crystallization process. To simplify the comparison, we used the time (t_{cm}) associated with the maximum rate of dE'/dt as an index of the crystallization rate. Therefore, a small t_{cm} corresponded with a fast rate of crystallization. At least four samples for each type of composite were tested to obtain the t_{cm}.

Figures 7 and 8 show the t_{cm} (average value and standard deviation) of aspen and maple composites, respectively. Both maple and aspen composites exhibited similar trends of crystallization rate. These two figures indicated that the MAPP crystallized faster than polypropylene and the polymer blends, which confirmed the observation from optical microscopy. The t_{cm} for the MAPP composites was 6 to 7 minutes, while the t_{cm} for the polypropylene and polymer blend composites was 12 to 14 minutes. Statistically, it was not possible to distinguish the crystallization rate of the polypropylene and polymer blends because the sam-

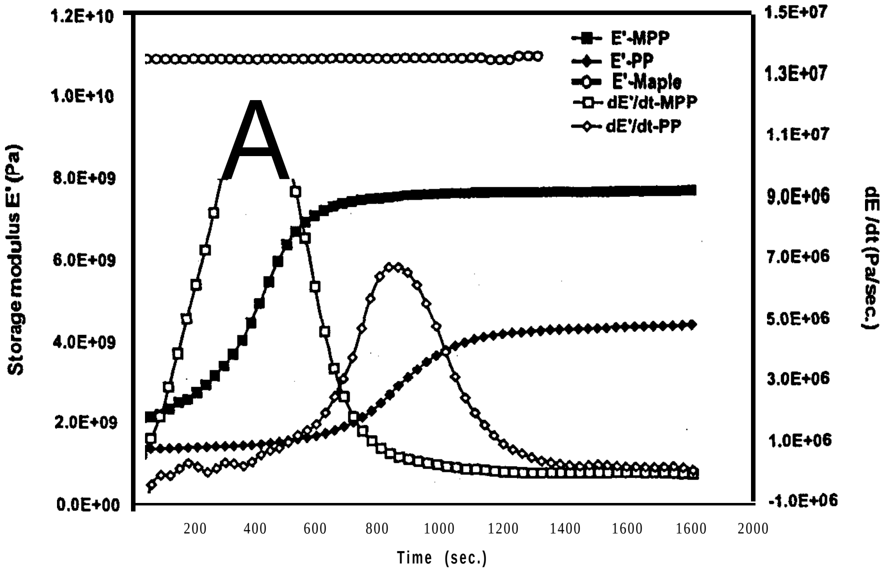

Figure 5. ~ Evolution of the storage *modulus of maple, maple-polypropylene, and maple-MAPP composites at 135°C.*

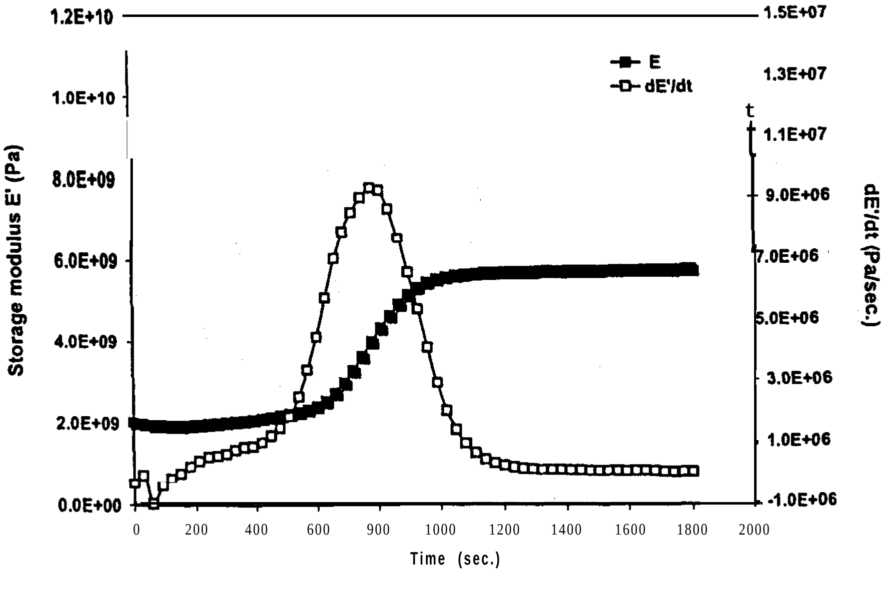

Figure 6. ~ ***Evolution of the storage*** modulus ***of the maple-polypropylene-MAPP (5%) composite*** at 135°C.

ple size was not big enough for an analysis of variance. Further study is needed to clarify the effect of the MAPP quantity on the crystallization process and mechanical properties of the composites.

Conclusions

From this preliminary study, the following conclusions could be made:

1. The nucleation ability of whole woodfibers for polypropylene is poor and the formation of a transcrystalline layer is not common around whole woodfibers.
2. The addition of a small portion of MAPP increases the nucleation capacity of woodfibers for polypropylene, and changes the crystal morphology of polypropylene around the fiber. When MAPP is added, surface crystallization dominates over bulk crystallization and a transcrystalline layer can be formed around the woodfibers.
3. The MAPP crystallizes faster than the polypropylene and polypropylene-MAPP blends in the presence of woodfiber and the addition of MAPP has little effect on the crystallization rate of polypropylene. Differential scanning calorimetry results were consistent with these observations.

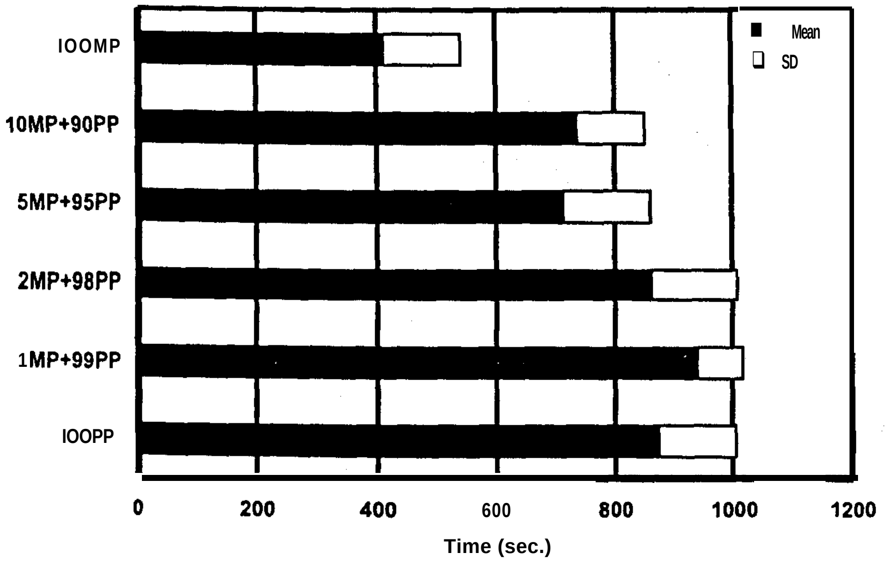

Figure 7. ~ *Time* (t_{cm}) *associated with* the maximum rate of *dE'/dt* for *maple composites.*

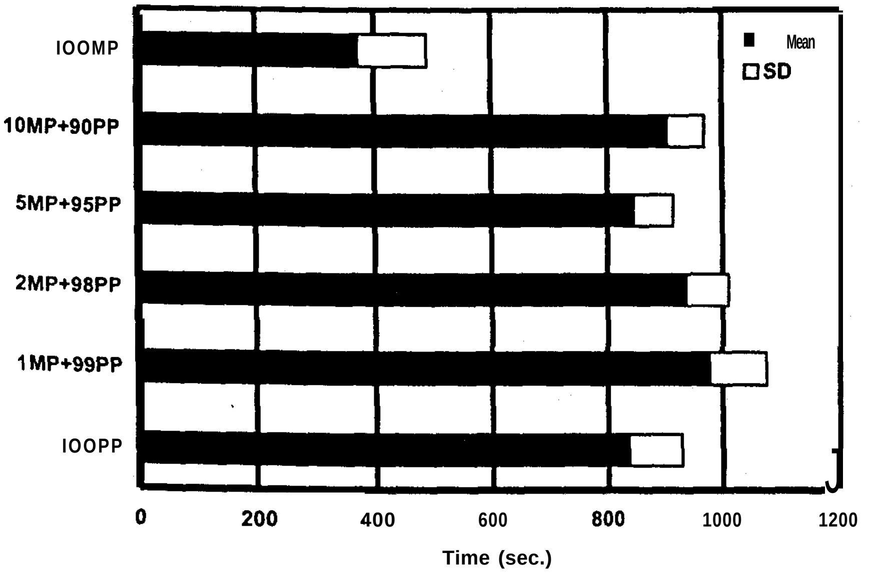

Figure 8. ~ *Time* (t_{cm}) *associated with the maximum rate of dE'/dt for aspen* composites.

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