

## Using dynamic mechanical spectroscopy to monitor the crystallization of PP/MAPP blends in the presence of wood

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**Abstract**—Crystal morphology of thermoplastics is known to be strongly influenced by the presence of solid substrates like fibers or fillers. For wood, this interphase development is governed by the chemical composition of the thermoplastic and substrate. The crystallization of PP/MAPP blends was observed using polarized light microscopy and quantified using DSC and DMA. Techniques are presented to assess degree of crystallinity and temperatures associated with the onset ( $T_G$ ) and maximum rate ( $T_C$ ) of crystallization using DMA. Strain history of the specimen during crystallization was evaluated and does not significantly influence either  $T_G$  or  $T_C$ . Crystallization temperatures of PP as assessed using DSC or DMA increase with the addition of MAPP or the presence of wood. Values for  $T_C$  are higher when measured by DMA than DSC. This difference appears to be related more to the relative interfacial dominance in the specimens, rather than to an inherent difference between techniques.

**Keywords:** Wood; polypropylene; maleic anhydride; dynamic mechanical analysis; transcrystallinity.

### 1. INTRODUCTION

Polyolefins are increasingly used in conjunction with wood and other ligno-cellulosic materials to produce hybrid composites. These materials possess thermal and mechanical efficiencies in processing that aid in producing a variety of sheet and hollow products. Because little natural interactions occur between these dissimilar materials, the development of an effective interphase has been of some research interest.

Semi-crystalline thermoplastics like polypropylene (PP) and high-density polyethylene (HDPE) are widely used in commercial wood/plastic composites. Male-

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ated polypropylene (MAPP) has been of substantial interest because it is widely available, inexpensive, and reasonably effective as a coupling agent for PP-based composites. Although wood-HDPE composites are more prevalent in the marketplace, similarly useful compatibilizers have not yet been adopted.

In synthetic composites, recent research has addressed the kinetics of crystallization using polarized light microscopy [1]. The role of transcrystallinity in these and wood/plastic composites [2-6] has been a dominant theme in the interfacial development. Unlike HDPE, the crystallization of PP is easy to observe because the crystal size is large enough to observe with conventional microscopy techniques. Focusing on the increases in mechanical properties resulting from crystallization provides a means of monitoring the kinetic process while not physically observing the results.

### 1.1. Objectives

While addressing the development of a wood/plastic interphase in PP-based wood composites, this research specifically:

1. Assesses the influence of MAPP on the crystallization of PP in the presence of wood.
2. Determines the viability of dynamic mechanical spectroscopy on wood/thermoplastic laminates to monitor and quantify crystallization.
3. Provides a quantitative comparison of crystal formation as studied using mechanical and calorimetric techniques.

## 2. MATERIALS AND METHODS

### 2.1. Sample materials and preparation

Commercially prepared polypropylene (PP, Exxon PP-7292W) and maleic anhydride-modified polypropylene (MAPP, Epolene G-3003) were used in neat and blended forms to study crystallization in the presence of wood. The powdered thermoplastics were hot pressed between glass plates to produce 0.1-mm thick films of predetermined composition. Films were produced from the neat PP and MAPP. In addition, the PP was compounded with 2, 5, and 10% blends of the MAPP. Thin (0.65-mm) aspen (*Populus spp.*) veneers were produced by knife milling and dried in an oven between glass plates at 103°C. Both the thermoplastic films and wood veneers were trimmed and used as produced.

Three-ply laminates were constructed to study polypropylene crystallization in the presence of a wood substrate. A single 0.1-mm thick polypropylene film was placed between two 0.65-mm thick wood veneers to assemble the laminates. The laminate assemblies were then hot pressed with nominal pressure at 200°C for 15 min. Following pressing, the laminates were rapidly cooled between glass plates and sized to 50 × 6 × 1.4-mm samples for DMA. The longitudinal axis of the wood veneers was oriented with the long axis of the DMA samples for all samples.

## 2.2. Dynamic Mechanical Analysis

DMA was conducted using a Rheometrics RSAII Solids Analyzer equipped with a dual-cantilever bending fixture. The fixture is designed to rigidly clamp the specimen ends and center to restrain angular rotation at these points. The clamps were secured via thumbscrews that were hand-tightened at two times during the experiment: (1) prior to loading at ambient conditions; (2) prior to cooling at 200°C. The sample is tensioned along the long axis via an internally mounted spring.

The center clamp fixture applies a sinusoidal oscillating load transverse to the long axis of the specimen. Vibration frequency and amplitude were varied for the different experiments. Mechanical energy is known to influence the crystalline state of polymers. In a DMA experiment, the total mechanical energy can be influenced by the imposed dynamic strain, frequency of oscillation, and period of mechanical excitation. To assess any potential influence that the mechanical testing conditions might impose on the crystallization results, two different strain histories were studied (Table 1). High and low levels of the test parameters were grouped to impose these conditions and are subsequently referred to as high-strain and low-strain histories.

During the DMA experiments, the temperature was raised rapidly from ambient to 200°C. Following a ten-minute conditioning period, the specimen was cooled to 150°C at 5°C/min, from 150 to 110°C at 2°C/min, and from 110°C to ambient at 5°C/min. The sample was vibrated either intermittently or continuously during cooling to collect data for computing the dynamic mechanical response. For samples excited intermittently, strain was applied only during the period required to collect data at 2°C intervals. A typical period would entail three cycles of vibration followed by a minimum of two cycles required for data collection and verification. Mechanical data were not collected during the initial temperature increase because the clamps would loosen resulting in invalid information.

During crystallization, the storage modulus ( $E'$ ) increases with decreasing temperatures between 150 and 110°C. Although the form of the increase was consistent among different samples manufactured with the same thermoplastic film type, the absolute values of  $E'$  for different samples differed in both the melted and crystallized state. This variability resulted from the natural variability evident in the wood substrate. To facilitate comparison, the response of each specimen was converted to

**Table 1.**  
DMA test parameters for conditions to impose low-strain and high-strain histories

Strain history	Low	High
Dynamic strain	0.0005	0.0010
Frequency (Hz)	1	10
Excitation	Intermittent	Continuous

a degree of crystallization ( $\chi_c$ ):

$$\chi_c = \frac{E'(T) - E'_{\min}}{E'_{\max} - E'_{\min}}$$

This calculation assumes that the storage modulus at any temperature ( $E'(T)$ ) relates to the crystalline state of the thermoplastic phase. The values for  $\chi_c$  will range from 0 to 1 corresponding to an absence and completion of crystallization. The minimum ( $E'_{\min}$ ) and maximum ( $E'_{\max}$ ) values for storage modulus were selected within the range of 110 to 150°C.

Six replicate samples were produced and evaluated for each thermoplastic blend studied. The average behavior of  $\chi_c$  was calculated by averaging the  $\chi_c$  value for each temperature among the six DMA samples. The rate of crystallization ( $d\chi_c/dT$ ) was calculated from each average  $\chi_c$  curve to quantify two characteristic temperatures, the onset ( $T_o$ ) and maximum rate ( $T_c$ ) of crystallization. The  $T_o$  value was selected as the temperature corresponding to a slope limit of  $-0.005/^\circ\text{C}$ . Likewise, the  $T_c$  value was selected as the temperature corresponding to the minimum observed slope value.

### 2.3. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC, Perkin-Elmer Model DSC-7) was used to confirm crystallization temperatures. Wood flour (40 mesh aspen), PP, and MAPP blends were created by compounding predetermined amounts of the materials in a laboratory twin-screw extruder. Samples of the compounded materials were placed in hermetically sealed DSC pans and subjected to a temperature ramp at  $10^\circ\text{C}/\text{min}$ . The temperature corresponding to the maximum heat flow was chosen as  $T_c$ .

### 2.4. Polarizing Optical Microscopy

Polarizing Optical Microscopy (POM) was used to visualize the crystalline structure of the thermoplastic phase. The transmitting light-microscope (Zeiss Universal) was mounted with a heated stage, polarizing filters, and a camera. To produce POM samples, slices of the wood-PP laminates produced for DMA, were taken from the laminate edge using a sliding knife microtome. The samples were then heated on the hot stage to  $200^\circ\text{C}$  and equilibrated for 10 min before cooling the stage to  $135^\circ\text{C}$  to induce crystallization. Crystalline structure was photographed using an attached camera.

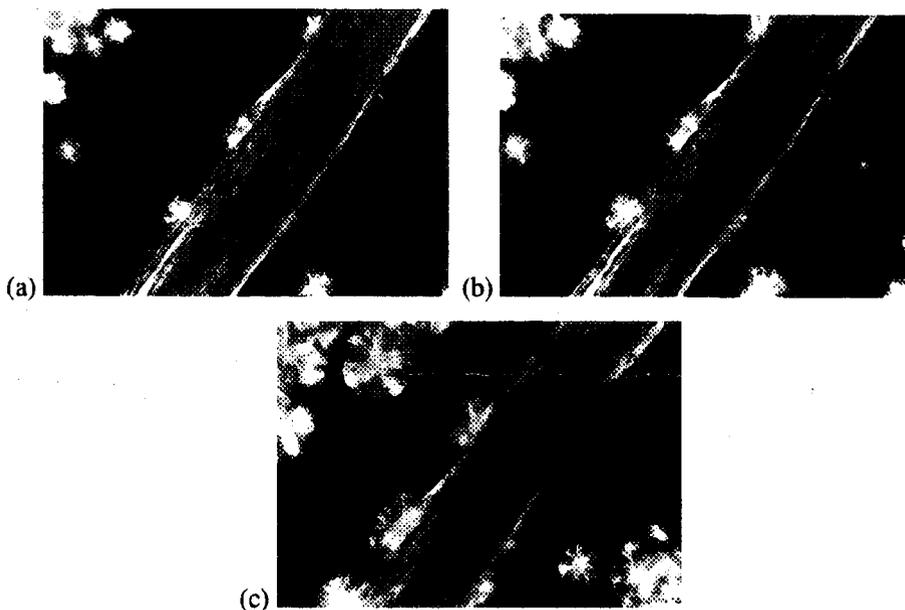
## 3. RESULTS AND DISCUSSION

Crystallization is the mechanism that controls hardening of many thermoplastic polymers. The crystallization process results in a mechanical response that corresponds to the hardening. However, both the substrate presence and the imposed

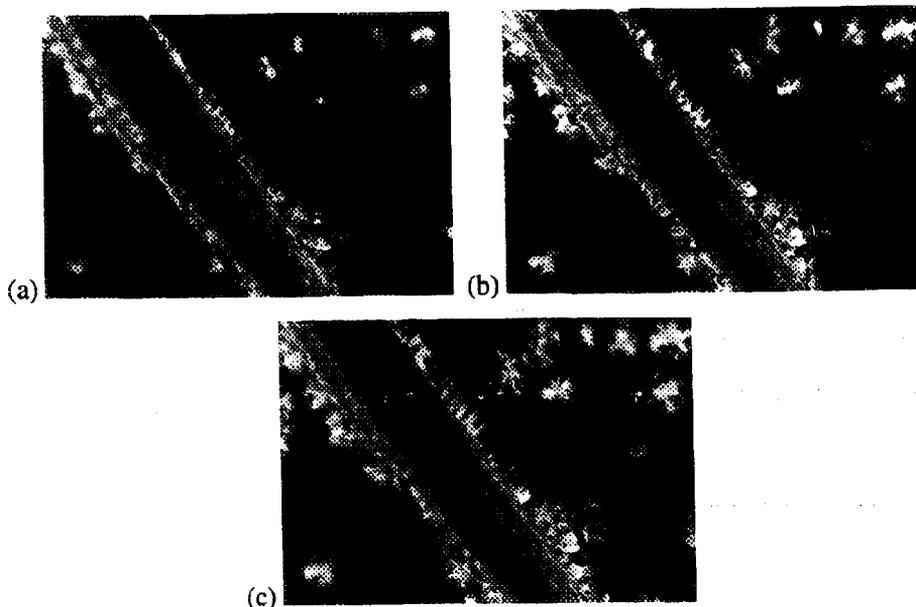
mechanical excitation can influence the crystallization process. Both of these variables must be studied to understand if DMA can be used to monitor the hardening process.

### 3.1. Polypropylene crystallization with wood

The crystallization of PP and MAPP films in contact with wood were observed using POM (Figs 1 and 2). Crystallization of thermoplastic phase is dominated by the formation of spherulites for both thermoplastics. Spherulites formed in the MAPP were smaller and more frequent than those in the PP. The most notable difference between the thermoplastics, however, was the presence of a prominent transcrystalline layer on the wood substrate with the MAPP. This layer was formed early in the crystallization process and was present even when the concentration of MAPP was as low as 2% in a blend with PP. Several researchers [2–5] have noted the formation of transcrystalline layers with polypropylene on cellulose or wood surfaces. This layer is prominent with the relatively clean cellulose surfaces found with bleached pulp [2, 3] and appears to be inhibited by other natural polymers such as lignin and hemicelluloses [3]. Although little research has addressed whole wood, these findings are consistent with those of various levels of bleached pulp [3].



**Figure 1.** Optical micrographs (actual dimensions  $1.5 \times 1.0$  mm) of PP melt crystallizing at  $135^\circ\text{C}$  in the presence of single wood fiber for (a) 10 min, (b) 15 min and (c) 20 min.



**Figure 2.** Optical micrographs (actual dimensions  $1.5 \times 1.0$  mm) of MAPP melt crystallizing at  $135^\circ\text{C}$  in the presence of single wood fiber for (a) 10 min, (b) 15 min and (c) 20 min.

### 3.2. Calorimetric measures of crystallization temperature and energy

Crystallization temperatures ( $T_c$ ) and energy ( $\Delta H_c$ ) as determined by DSC are shown for neat and blended PP and MAPP (Table 2). In addition, the polymers were compounded with 30% wood flour. In the unfilled state, the  $T_c$  of neat PP is higher than either MAPP or PP/MAPP blends. The total energy consumed during crystallization ( $\Delta H_c$ ) is higher for the neat PP than MAPP, but is minimum and relatively invariant for all of the PP/MAPP blends.

Both the  $T_c$  and  $\Delta H_c$  of the thermoplastics change when compounded with 30% wood flour. When compared with the unfilled PP, the  $T_c$  and  $\Delta H_c$  decrease with the wood-compounded PP. In contrast, the presence of wood flours causes the  $T_c$  and  $\Delta H_c$  to increase for the neat MAPP and PP/MAPP blends. This increase is largest for the neat MAPP and may reflect the influence of the transcrystalline layer. Transcrystalline layers form around included fibers or particles when the nucleation density becomes sufficiently high to cause embryonic spherulites to impinge upon neighboring domains [7]. A highly ordered crystalline layer forms transverse to the substrate. For PP and wood, this high degree of order appears to result in an increased crystallization temperature and energy when compared to unfilled thermoplastics.

**Table 2.**

Influence of wood on the calorimetric measure of crystallization temperature ( $T_c$ ) and energy ( $\Delta H_c$ ) for neat and blended PP/MAPP

MAPP (%)	Unfilled polymer		Filled polymer (30% Wood)	
	$T_c$ ( $^{\circ}\text{C}$ )	$\Delta H_c$ (J/g)	$T_c$ ( $^{\circ}\text{C}$ )	$\Delta H_c$ (J/g)
0	115.1	-108.3	113.6	-86.1
2	111.0	-83.6	116.9	-86.0
5	111.6	-84.9	116.1	-84.2
100	112.9	-91.6	119.3	-93.8

### 3.3. Mechanical measures of crystallization

When it is examined using DMA, the crystallization process is evidenced by a rapid increase in storage modulus,  $E'$ , from the melt to the solidified plateau values (Fig. 3). The  $\chi_c$  vs. temperature curve has a similar appearance except the plateaus are at fixed values of 0 and 1 (Fig. 4). Direct comparison of the curves can be used to qualitatively assess the influence of variables on the crystallization process. In addition, direct measures can provide quantitative comparison for the onset and peak of crystallization.

In general, MAPP laminates crystallize at higher temperatures than those produced with PP. The addition of low levels of MAPP to PP films moves the crystallization process to increased temperatures proportional to the MAPP level. When the laminates produced with a neat PP and MAPP are compared, the largest difference appears in the early (high temperature) regions of crystallization.

### 3.4. Mechanical metrics for crystallization

Temperatures corresponding to the onset ( $T_0$ ) and maximum rate ( $T_c$ ) of crystallization can be quantified by calculating the slope  $\chi_c$  with respect to temperature ( $d\chi_c/dT$ ). With POM or DSC, induction time is typically recorded as a measure of the first nucleation event. Surely DMA lacks the sensitivity to measure the first nucleation, but the onset of hardening can be reliably assessed. Likewise, the  $T_c$  was chosen as the minimum slope for the  $E'$  vs. temperature curve.

As with the calorimetric measure, the DMA measure of  $T_c$  for MAPP and PP/MAPP blends are higher than that of neat PP. Strain history had little influence on the value of  $T_c$  measured using DMA (Table 3). However,  $T_0$  of the PP and 2% MAPP laminates appears to be more sensitive. Pogodina *et al.* [8] found a significant influence of strain history when measuring the evolution of shear storage modulus ( $G'$ ) with crystallization of isotactic PP (iPP). However, the physical construct of these experiments differed substantially from this research.

The actual value of  $T_c$  is higher when measured with DMA than with DSC. Researchers [9] have noted similar relationship between calorimetric and mechanical measures of cure temperatures of thermosetting polymers. In thermosetting

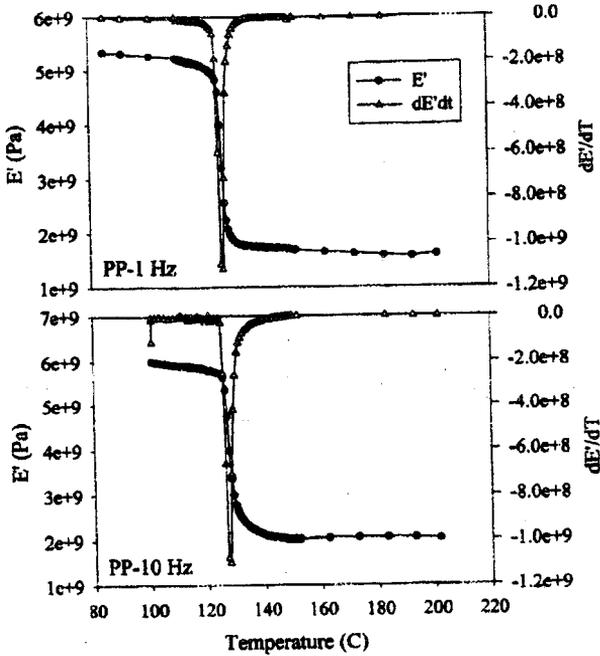
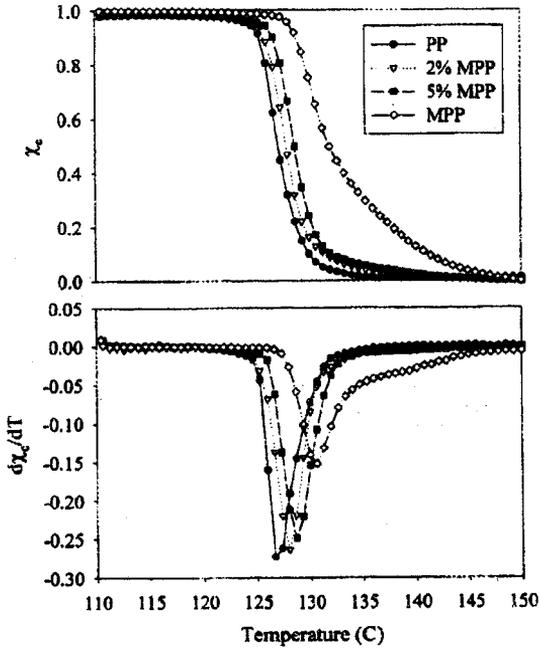


Figure 3. Dynamical mechanical spectra for wood/poly(propylene) laminate under cooling. Both the storage modulus ( $E'$ ) and slope ( $dE'/dT$ ) are shown.

crosslinked polymers, this behavior is usually attributed to the fact that low levels of crosslink density have little influence on mechanical behavior but has equal influence on heat flow [10]. Relating the hardening process of crystallization to the cure of thermosetting resins, recall that in cooling experiments, the higher value of  $T_c$  corresponds with the *early* stages of hardening, opposite of the heating experiments used in cure of thermosets. Therefore, one might interpret the difference in  $T_c$  to suggest that the early stages of crystallization have a stronger influence on the hardening process than does the latter. Pogodina *et al.* [8] equated crystallization of iPP to gelation of a thermosetting resin where gelation occurred in the first 5–10% of the increase in  $G'$ . Equating this conclusion to cure of thermosets would imply that the majority of increase for mechanical performance in the thermoplastic laminate occurs after gelation, similar to thermosetting resins. The imposed mechanical strain used in the DMA may also increase the measured  $T_c$ ; however, the results of strain history do not support this hypothesis.

The most plausible explanation to relate the  $T_c$  determined using DMA and DSC is the relative contribution of the interface in the specimens used for the two experiments. The DSC results showed that the presence of wood increased the  $T_c$  and  $\Delta H_c$  of the thermoplastic, suggesting an interfacial interaction that produces a preferentially ordered crystalline morphology (i.e. transcrystallinity). In fact, the



**Figure 4.** Degree of crystallinity ( $\chi_c$ ) and rate of crystallization ( $d\chi_c/dT$ ) curves for wood laminates produced with PP/MAPP blends. The DMA was conducted using parameters corresponding to a low strain history.

**Table 3.**

Temperatures corresponding to the onset ( $T_0$ ) and maximum rate ( $T_c$ ) of crystallization as determined using DMA

MAPP (%)	Low strain history		High strain history	
	$T_c$ (°C)	$T_0$ (°C)	$T_c$ (°C)	$T_0$ (°C)
0	127	134	127	141
2	128	137	128	142
5	129	141	129	142
100	131	150	131	149

dominance of interfacial region in the laminated specimens may have accentuated this effect, driving the  $T_c$  higher than that measured by DSC.

#### 4. CONCLUSIONS

The hardening process of PP is influenced by the presence of wood. The contribution of MAPP is to promote the formation a transcrySTALLINE layer in the

wood/plastic interphase. The presence of this layer appears to substantially increase all measures of the crystallization process.

Dynamic mechanical analysis can be employed as a tool to monitor the crystallization of thermoplastics in the presence of wood. This technique provides a qualitative and quantitative assessment of the hardening process incurred during cooling. Differences in the magnitude of  $E'$  were influenced by the natural variability in the wood substrate. A normalization technique was used to calculate the change in degree of crystallinity ( $\chi_c$ ) with cooling. The temperature associated with both the onset ( $T_o$ ) and peak rate ( $T_c$ ) of crystallization can be calculated using  $\chi_c$ .

Crystallization temperatures ( $T_c$ ) determined using DMA were higher than those from DSC. Results produced to study the influence of mechanical strain do not explain this effect. The effect is most likely attributed to differences in the contribution of the wood/plastic interphase in the sample.

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