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The Rheology and Extrusion Processing Performance of Wood/Melamine Composites

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ABSTRACT: A modified melamine resin that exhibits both thermoplastic and thermoset behaviors was used as a matrix for wood plastic composites (WPCs). The thermoplastic melamine (TPM) resin exhibits a glass transition at approximately 34°C and continues to be thermally malleable until a crosslinking reaction develops with additional heating and an acid catalyst. Varying blends of TPM and wood flour were evaluated for their rheology and curing behavior using torque rheometry. WPC composites were manufactured with extrusion methods and final product properties determined. The torque rheometry results showed a highly dependent relationship of the curing behavior to the amount of wood flour utilized and temperature. Based upon the torque rheometry results, two extrusion platforms were developed to initiate the curing process; (1) cure within the die land and (2) post-cure of the extrudate. The post-cure procedure provided composites with higher mechanical properties. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39858.

KEYWORDS: cellulose and other wood products; composites; crosslinking; extrusion

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INTRODUCTION

Wood plastic composites (WPCs) generally are comprised of thermoplastic resins, with polyethylene, polypropylene being the most commonly utilized matrices. These composites are limited in strength and stiffness and are often susceptible to high levels of creep.[1–3] Thermoset composites provide a crosslinked structure that imparts better creep performance and improve fire and heat resistance that would be a strategic benefit in the field of WPCs. However, thermosets generally require different processing platforms that accommodate low viscosity resins and the cure kinetics of the crosslinking reaction. These processing methods can potentially limit the production rates and negate the economic feasibility to produce certain profiles and shapes.

A modified thermoset melamine resin has been developed (Borealis Agrolinz Melamine GmbH) to exhibit both a thermoplastic and thermoset phase. The thermosetting reaction relies on an acid catalyst and is accelerated with elevated temperatures. The etherified thermoplastic melamine (TPM) was developed by incorporating polymer/oligiomer chains between the melamine resin molecules.[4–6] A more comprehensive review of the reaction scheme of melamine resins and the studied TPM is illustrated by Bauer[7] and Bergmann et al.,[8] respectively. The polymer chains were designed to allow the resin to become malleable at elevated temperatures prior to the initiation of the crosslinking reaction. With this addition, these TPMs can be utilized on thermoplastic processing equipment, such as extrusion and injection molding. However, understanding the processing rheology coupled with the cure kinetics is crucial to minimize processing pitfalls and maximize the composite performance.

Previous work by Braun et al.[4] looked at formulations of the TPM resin with differing reactivities, which altered the processing window. The TPM resin with a quicker onset of cure showed a more complete reaction but with a much reduced processing window. The presence of wood, primarily the lignin and hemicelluloses, provided the acidic catalyst to cure the melamine resin.[8] Sommer and Fritz[6] incorporated flax fibers with boric acid to control the curing reaction. Their results showed an increased kneader time and improved flexural strength when boric acid was added to the formulation. Haider et al.[9] showed improved performance of TPM wood composites when exposed to higher temperatures when compared to polypropylene-based WPCs.

Recent work by Haider et al.[10] has addressed more of the processing parameters associated with extruding these TPM–wood systems. Their work showed much promise for producing WPCs based on these plasticized melamine resins; however, processing parameters will play a large role in the integrity of the final product.

To evaluate this TPM for conventional polymer processing the thermal attributes need to be characterized. The following

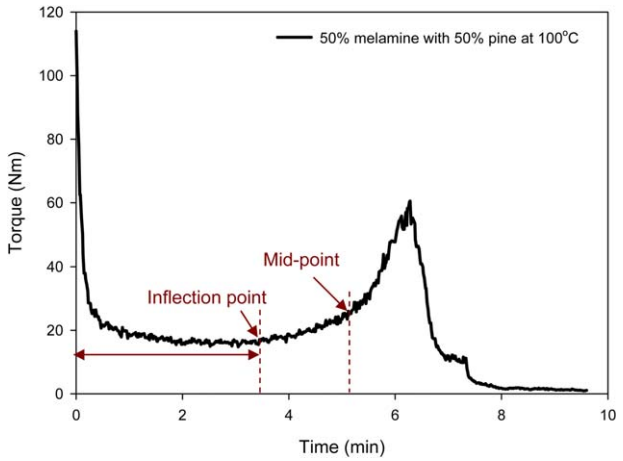

Figure 1. Typical torque curve for the wood–TPM blend illustrating the inflection and mid-points indicating the onset of cure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

research addresses the thermal degradation, kneading, and curing behavior of the TPM/wood composite. Extrusion platforms were developed that accommodate the kneading and melt-blending attributes and the subsequent cure of the TPM–wood composite. These platforms were devised to initiate cure within the extrusion process and for a post-cure annealing step to complete the crosslinking reaction.

MATERIALS

The TPM resin (HIPE®ESIN, type MPER 4.0 T5 E) was acquired from Borealis Agrolinz Melamine GmbH as a dry particulate. The wood flour used was a commercial 60-mesh eastern white pine (*Pinus strobus*) obtained from American Wood Fibers®. The wood-melamine-resin compounds were mixed as neat TPM resin with wood flour, on a weight-basis.

Methods

Thermal Decomposition. The neat TPM resin was analyzed for thermal degradation behavior with thermal gravimetric analysis (TGA). Samples of approximately 10 mg were placed in an aluminum crucible and exposed to a heating rate of 10 °C/min over a temperature range of 30–600°C. Nitrogen gas was used as the inert purge gas in order to avoid unwanted oxidation of the sample.

Thermal Transition. Differential scanning calorimetry (DSC) was used to determine the thermal transition, potentially the glass transition (T_g) of the TPM resin prior to being cross-linked. The uncured TPM was ground with a Wiley mill using a 40 mesh screen and conditioned in a desiccator for 24 h at ambient temperature. DSC scans were then performed on 5 mg samples heated from −40°C to 100°C at a heating rate of 20 °C/min in hermetically sealed 40-μL aluminum crucibles. The same sample was scanned twice, first to remove any thermal history, while the second heating scan was used for evaluation.

Torque Rheometry. A torque rheometer was used to evaluate the melt-blending and curing characteristics of wood–TPM composites at various temperatures and wood flour levels. Roller rotors were utilized as mixing elements for the rheometer and all tests were performed at a screw speed of 50 rpm.

The torque rheometry curves were used to characterize the curing behavior by calculating inflection points and mid-points of the torque curves. The inflection point represents the onset of the cure and the mid-point was used to characterize a more fully developed cure (Figure 1). In order to determine these points, the torque curve was fitted to a 4th order polynomial, which was then used to calculate the inflection and midpoints. The decay from the initial torque observed during the closure of the torque rheometer chamber was omitted in the fitted curve, along with the final decay of torque after the composite cured and began to deteriorate.

Extrusion. A 35-mm conical counter-rotating twin-screw extruder at a screw speed of 10 rpm was used to process a 38 mm × 10 mm rectangular profile composite. At 10 rpm, the dwell time of the material in the extruder and dies is roughly 3–5 min depending upon the temperature and formulation. Composition of the extruded WPC was 50% wood flour, 47% melamine resin, and 3% oxidized polyethylene for lubricant (Honeywell 629A) on a weight-basis. Based upon the torque rheometry data, six different temperature profiles (A–F) were used to extrude the WPC. Processing temperatures were independently controlled in three barrel zones, two die zones, and the screws (Table I). A schematic of the extrusion barrel and die zones can be seen in Figure 2. Applied vacuum venting in Barrel Zone 2 was also used to remove volatiles during extrusion (Figure 2). The temperature profiles D–F represent a manufacturing

Table I. Extrusion Temperature Profile and Processing Parameters for the TPM-Based WPCs

Temperature (°C)	A	B	C	D	E	F
Barrel Zone 1 (Feed)	60	66	71	102	102	102
Barrel Zone 2	64	71	80	105	105	105
Barrel Zone 3	66	71	80	105	110	110
Die Zone 1	82	80	80	105	116	116
Die Zone 2	88	88	93	121	140	140
Screws	65	71	80	102	108	116
Process Parameter						
Melt Temperature (°C)	83	82	91	109	118	120
Melt Pressure (psi)	1342	1368	1050	342	333	590
Screw Speed (rpm)	10	10	10	10	10	10

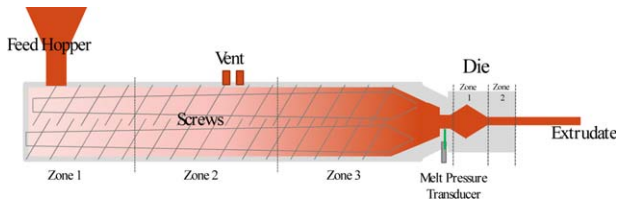

Figure 2. Overall schematic of the temperature zones on the twin-screw extruder and die. Screws were heated using oil and the temperature was measured at the infeed distributor block. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

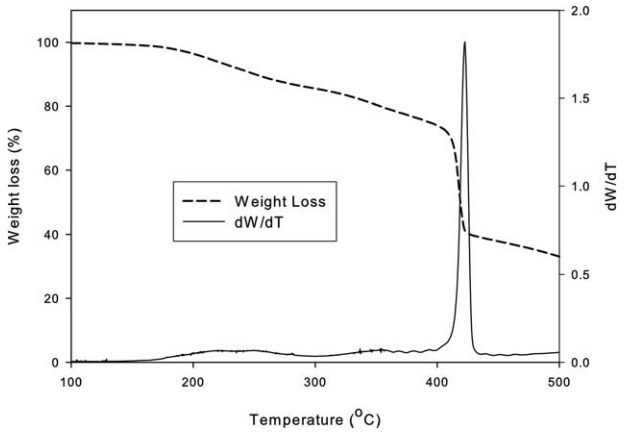

Figure 3. TGA cure of the TPM resin.

platform to cure the composite during extrusion. Profiles A–C were developed to extrude a melt blended uncured composite that would require a post-heating step to initiate cure. This two-stage processing methodology is similar to the work by Sommer and Fritz[6] where a melt-blend of the flax and melamine resin was initial performed followed by a separate compression or injection molding step.

Post-extrusion heating was utilized to ensure a complete cure of all melamine within the six temperature profiles. Specimens for each group were heated in a convection oven at 175°C for 6 h. After post-heating, the samples were stored in a 20°C and 50% relative humidity conditioning room for at least 48 h prior to any further tests. Specimens that had no post extrusion heating were placed directly into the 20°C and 50% relative humidity conditioning room.

Mechanical Testing and Statistical Evaluation. The conditioned specimens were then subjected to flexure testing procedures, where ASTM D-790[11] was followed. The modulus of elasticity (MOE), modulus of rupture (MOR), and the strain at the time of the composite break were calculated from the load and deflection data acquired in real-time. An analysis of covariance (ANCOVA) was used to evaluate the flexural properties of the extruded composites with density acting as a covariate.

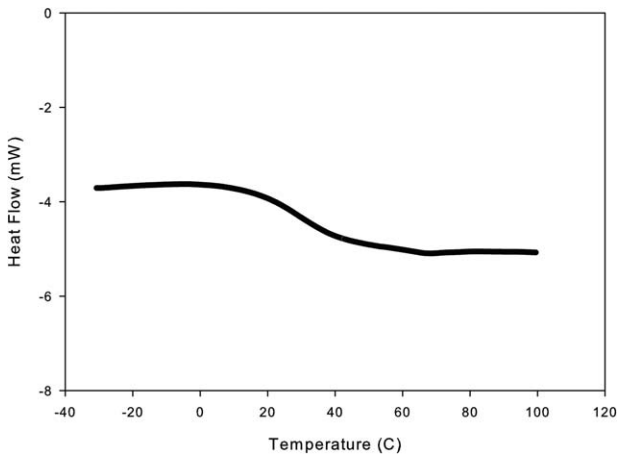

Figure 4. DSC curve of the neat TPM showing the T_g region.

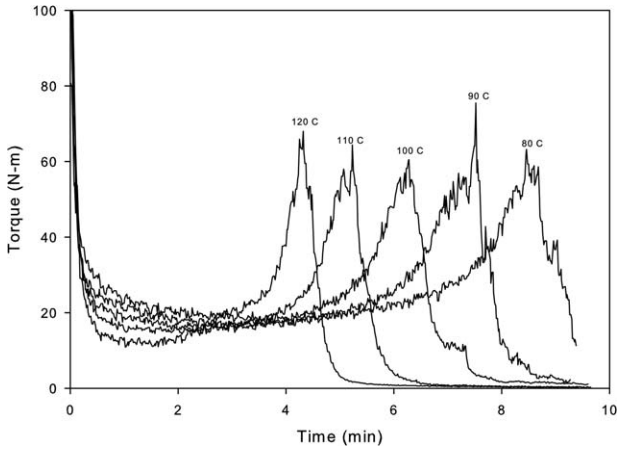

Figure 5. Torque rheometry curves for the wood/TPM composites at varying temperatures (50% wood content).

RESULTS AND DISCUSSION

Thermal Analysis

The results from the thermal degradation tests show little weight loss until after 175°C of the neat TPM, approximately 1% by 180°C (Figure 3). The absence of degradation within the thermoplastic region is beneficial for processing non-cellular composites. Irregular and uncontrollable decomposition of gases during processing can create voids and alter the melt viscosity causing problems with composite integrity. The derivative of weight loss with respect to temperature (dW/dT) provides a more detailed description of the thermal degradation with the most pronounced peak above 400°C. No wood or acid catalyst was added to the TGA samples, so a curing reaction did not occur.

The observed T_g of the TPM resin was found to be 34.5 ± 0.07°C within the three replicates run on the DSC. Figure 4 shows a representative curve with a very distinct shoulder with the value of the T_g determined by the midpoint of the transition period. This transition is likely not of the melamine itself due to the lack of an acid catalyst, but of the molecular chain that connects the melamine and provides the thermoplastic

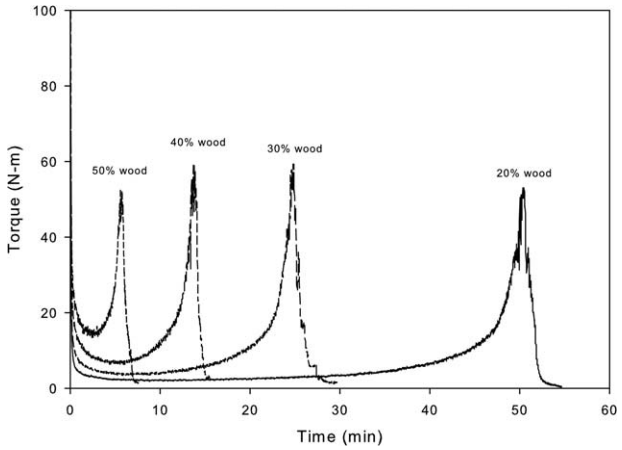

Figure 6. Torque rheometry curves for the wood/TPM composites at varying wood contents (100°C temperature).

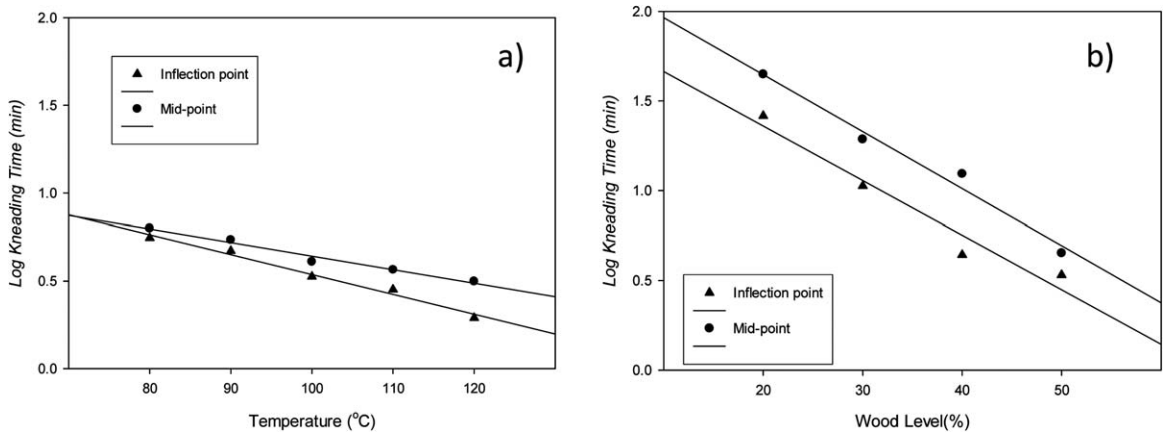

Figure 7. The inflection and mid-point data from the torque rheometry tests, based upon the chamber temperature (a) and wood filler level (b).

attributes of the resin and its ability to be formed into a profiled shape. In an uncured state a typical melamine resin has a T_g of approximately 70°C, although this can be difficult to observe, however the T_g of a cured melamine resin can be anywhere from 130 to 180°C, varying primarily to the chemistry and catalyst level.[12] Noting where this softening point or T_g occurs for the thermoplastic chain is important when developing temperature profiles for processing in order to create a malleable material.

Torque Rheometry Analysis

Torque rheometry results reveal the strong influence of wood content and temperature on the curing behavior of the TPM composite. Similar results for different material parameters were found by Braun et al.[4] and Sommer and Fritz.[6] In Figure 5, an increase in temperature resulted in a quicker onset of cure as observed by the increase in torque at a much reduced time frame. The same behavior can also be seen with wood content (Figure 6), as more wood was added to the formulation, the quicker the onset of cure. The increased contribution of the acidic groups with higher wood loadings accelerated the curing reaction. Once the TPM reached a cured or vitrified state, a decrease in torque was observed as the composite began to deteriorate and break apart due to the rotor action. Figure 7(a,b) indicates that onset and midpoint of cure follows a logarithmic relationship with temperature and time, respectively. In the temperature and wood level range that was studied, the concentration of wood in the blend caused the most significant influence on the curing behavior as indicated by the slopes of the curves in Figure 7(a,b).

Based upon the influence of wood level and temperature on the curing behavior, extrusion processing parameters must be tailored to accommodate this reaction. A temperature profile or wood content that is too high will result in an early onset of cure where there is a potential for the melamine bond, and the final composite, to be compromised. The steep drop in torque after the cure is complete and is indicative of a breakdown of the cured composite structure. The composite should also exit the screws and barrel prior to the onset of cure so that the mixing and pumping action of the screws does not disrupt the bonding mechanisms and diminish the final properties of the composite. With a 50% wood flour level (Figure 6) and an estimated dwell time of 3–5 minutes, one can see through Figure 5 when the curing reaction will likely occur at various temperatures.

Extrusion Results

The results in Figure 8 show that the melt pressure decreased as the temperature profile increased, which is due to the softening of the TPM composite material. However, in the highest temperature profile (F) there was a slight increase in melt pressure. This increase is likely due to some initial crosslinking which occurred in the extrusion barrel or dies from the higher temperatures. Temperature profiles E and F were quite similar except for F had an 8°C increase in screw temperature. This slight difference is quite apparent in the development of melt pressure.

The flexural stiffness (MOE) of the various extruded TPM/wood composites is shown in Figure 9. The ANCOVA results show a significant effect of the post-curing procedure and the extrusion temperature profile on the MOE. Without the post-curing procedure the results were quite variable throughout the range of the extrusion temperature profiles; however with the post-cure for 6 h at 175°C, the results became less sporadic and variable. Although there was statistical significance with the application of

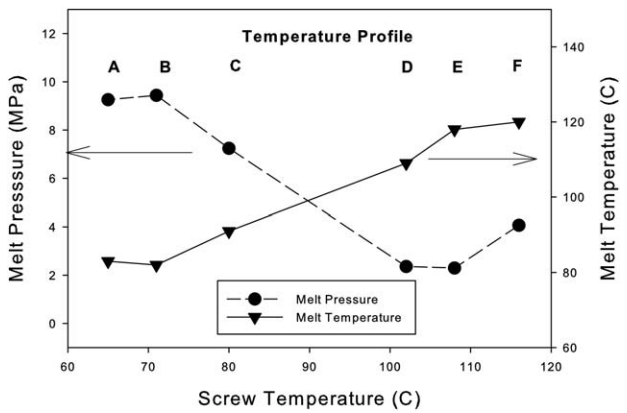

Figure 8. Processing variables of melt pressure and temperature for different extrusion temperature profiles.

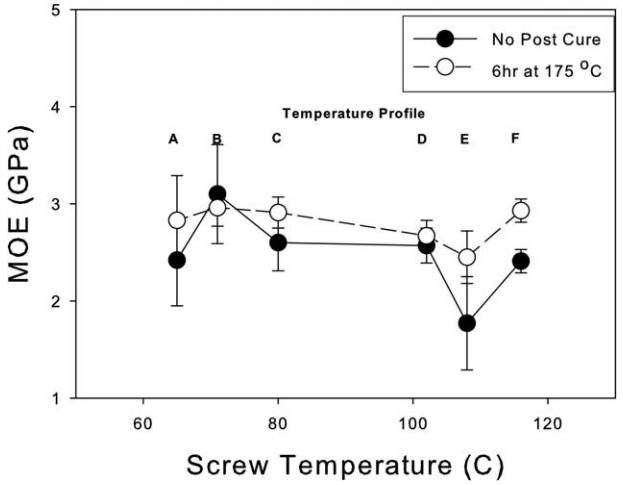

Figure 9. Flexural stiffness (MOE) of the extruded wood/TPM composites at the six temperature profiles.

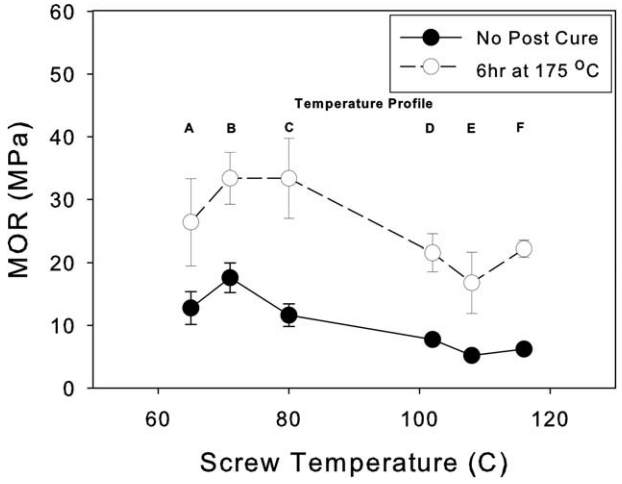

Figure 11. Flexural strength (MOR) of the extruded wood/TPM composites at the 6 temperature profiles.

the post-cure procedure and the extrusion temperature profile, the results appeared to show only a slight influence on the stiffness of these composites. For the measured strain at break (Figure 10), the post-cure process showed a significant increase in ductility or higher strains at break when the specimens were exposed to the 175°C post-cure process. There also appears to be a downward trend of strain at break as the temperature profile increased, where profiles E and F showed the lowest values for the post-cure specimens (Figure 11).

The most significant influence of the processing variables was found in the strength (MOR) of the specimens. In all temperature profiles, there showed an elevated MOR when the 175°C post-cure procedure was implemented, where some profiles showed a 200% increase. From these results, keeping a lower extrusion processing temperature and initiating cure after exiting the die (A–C) showed the highest overall mechanical performance of the composite.

The use of TPM resins as a matrix for WPCs shows much promise; however, the rheology along with the cure kinetics is both mutually critical in the successful process and final product performance. To maximize the potential properties and applications of TPM-based WPCs, identifying which variables will influence the desired properties is needed.

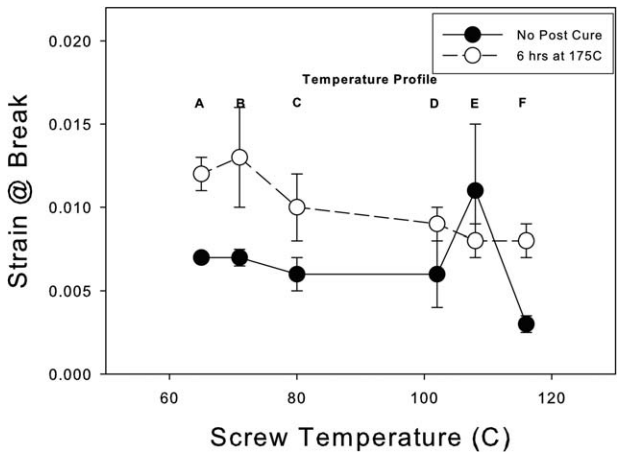

Figure 10. Strain at break for the extruded wood/TPM composites at the six temperature profiles.

The torque rheometry data revealed the influence temperature and wood filler levels had on the curing behavior of the composite system. As expected, higher temperatures decreased the time to cure, but more dramatically was the influence of wood filler level on time to cure. Low levels of wood flour (20%) resulted in onset of cure times to reach over 30 min at 100°C. This is compared to the 50% wood level which only took around 3 min to initiate cure. This influence is due to the acidic groups within the wood that catalyzes the melamine cure. In contrast, over the temperature range of 80–120°C, the onset of cure was only separated by 4–5 min for the 50% wood filler loading composites, clearly showing a higher dependency upon wood content than with temperature (Figures 5 and 6).

With the information developed by the torque rheometry data, a processing scheme was initiated to extrude the TPM-based WPCs. At 10 rpm, the 35 mm extrusion set-up takes 3–5 min for the material to be fed and pass through the die. Based upon the extrusion dwell time, the accelerated cure of the 50% wood filled system was used to generate the two processing platforms of curing in the die and post-curing after extrusion. The higher Die Zone 2 temperatures in profiles D–F of 121 and 140°C were set to enable cure to occur within the profile die; however, based upon much of the mechanical property evaluation, there was likely some damage accumulating in the barrel due to the action of the screws on a potentially crosslinking system.

CONCLUSION

The development of a TPM resin provides the ability for a thermoset system to be processed with the more robust and economical thermoplastic processing platforms (extrusion, injection molding, etc…) due to its thermally responsive behavior. Meanwhile the crosslinking attributes of the melamine reaction creates a potentially stronger binder for WPCs. The torque rheometry data shows a strong dependency on cure related to the amount of wood fiber utilized, due to wood's acidic nature

catalyzing the melamine reaction. Understanding the relationship of wood level and temperature on the curing kinetics is crucial for developing a robust processing platform. The results in this work show that extrusion processing require that limited curing behavior should incur during the mixing/kneading steps. The results show that maintaining a temperature profile that allows for the softening of the TPM, but does not induce a curing reaction during extrusion, followed by a post-heating procedure to be the most conducive for maximizing the mechanical properties of the WPC.

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