Fungal Degradation of Wood-Plastic Composites and Evaluation Using Dynamic Mechanical Analysis

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Received 6 December 2004; accepted 17 May 2005
DOI 10.1002/app.22945
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Small samples of two wood–polyethylene (HDPE) composite formulations were incubated with either the white-rot fungus *Trametes versicolor* or the brown-rot fungus *Gloeophyllum trabeum* for 24 and 77 days in an agar-block test. Noninoculated, side-matched controls were employed in the tests to serve as references, and solid wood samples of yellow-poplar (*Liriodendron tulipifera* L.) inoculated with *T. versicolor* were included as positive controls. Potential changes in storage and loss moduli because of fungal colonization and moisture were determined using dynamic mechanical analysis, whereas weight loss and visual observation served as indicators of fungal decay. Severe losses in storage modulus (E') and loss modulus (E'') following incubation of yellow-poplar with *T. versicolor* were observed. However, the E' of the two wood–plastic composite (WPC) formulations increased after 24 days of incubation with *T. versicolor*. The same effect was observed for *G. trabeum*, but only in one formulation. The increase of E' was attributed to a reinforcing effect of the fungal hyphae present in the interfacial gaps between the wood filler and the polymer matrix. Dynamic temperature scans revealed a peak in E'' between 30°C and 63°C, depending on the frequency and fungal treatment. The peak temperature of E'' represents the α-transition of HDPE. Increased activation energies were required for the α-transition in WPC samples incubated with *T. versicolor* for 77 days as compared to controls. This observation confirmed that incubation of WPC with *T. versicolor* improved interfacial adhesion and reinforced the composite under the assay conditions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3138–3146, 2006

Key words: activation energy; composites; degradation; extrusion; polyethylene (PE)

INTRODUCTION

Wood–plastic composites (WPC) have been manufactured in the United States for several decades but have only recently experienced significant market growth.[1,2] Although certain composite formulations demonstrate inherent resistance to fungal decay,[3] the presence of the wood filler presents some concern for the long-term decay susceptibility of WPC. Overall, detailed studies of fungal durability of WPC are limited,[4–9] and no standard laboratory tests have been developed to specifically test for fungal decay of WPC. The objective of this investigation was to evaluate if dynamic mechanical analysis could be used as an accelerated test method for the evaluation of fungal decay in WPC.

Dynamic mechanical analysis has been used extensively to characterize synthetic composite materials as well as wood and wood products.[10–17] It has also been employed as a technique to study fungal degradation of wood[18,19] and to investigate the chemical and physical effects of biopulping.[20] Dynamic mechanical analysis (DMA) potentially can provide valuable molecular and morphological information about a material in the solid state by subjecting it to dynamic loads over a broad range of temperatures and frequencies.[21] During measurement a sinusoidal strain is applied to the sample while measuring the sinusoidal stress response. A portion of the response output is in phase with the strain input and represents the energy stored in the material or the elastic component. The remaining response is out of phase with the strain and represents the energy dissipated by the material or the viscous component. A significant advantage of DMA over commonly used static mechanical strength tests is that incubation times in fungal decay experiments can be drastically shortened because of the employment of very small samples.

Relaxation transitions in high- and low-density polyethylene (PE) have been investigated extensively.[21–24] Transitions in polymers are labeled as α, β, γ, and so forth in alphabetical order with decreasing temperature.[23] Polyethylene shows clearly resolved peaks for α-, β- and γ-transitions.[23] The γ-transition corresponds to the glass-transition temperature of PE,[21,22] whereas the α-transition corresponds to molecular segmental motion in the crystalline phase, that is, chain rotation.[21] The

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α-relaxation in PE is often considerably modified, appearing to consist of at least two processes with different activation energies.[23] In high-density polyethylene (HDPE), the β-transition is usually absent.[24] For WPC exposed to wood decay fungi, it is desirable to understand if the α-transition is changed as a result of fungal degradation of the wood filler in the composite and to compare activation energies required for this transition in fungal-incubated and untreated WPC specimens.

In summary, this study was conducted to determine potential changes in the storage modulus (E'), loss modulus (E''), and dry weight of WPC and yellow-poplar following 24 and 77 days of incubation with a white- and a brown-rot fungus. It was anticipated that the results could be used to establish which parameter (E', E'', or dry weight) is most sensitive to evaluating fungal decay in WPC. In addition, activation energies required for α-transition in selected fungal-incubated WPC specimens and controls were calculated and morphological changes of WPC following incubation with wood decay fungi examined.

EXPERIMENTAL

Materials and composite preparation

The WPC formulations used in this study were selected from previous research that investigated the role of formulation components and design on biodegradation properties.[3] Specifically, formulations 3 and 7 from this previous study were selected, as they showed particular resistance and susceptibility, respectively, to fungal attack. For each formulation, maple (*Acer spp.* L.) 40-mesh wood flour (American Wood Fibers 4010, Schofield, WI) was used as a filler, and high-density polyethylene (HDPE) powder (Equistar Chemical LB010000, Houston, TX) served as the thermoplastic matrix material. Formulation 3 was composed of 49% wood filler and 45% HDPE, whereas formulation 7 consisted of 70% wood filler and 24% HDPE. Process additives were maintained at 6% (by weight) in both formulations and included ethylene bis-stearamide wax (General Electric Specialty Chemicals, Parkersburg, WV), zinc stearate (Chemical Distributors Inc. DLG20, Portland, OR), phenolic resin (Plenco 12631, Sheboygan, WI), and methyl diisocyanate resin (Bayer Mondur 541, Pittsburgh, PA). Side-matched yellow-poplar (*Liriodendron tulipifera* L.) sapwood samples were included in the study to serve as positive controls.

The components of each WPC formulation were mixed in a drum blender for 10 min and added to the feed hopper of a 55-mm counterrotating, conical twin-screw extruder (Cincinnati Milacron, Batavia, OH). A slit die (15.24 by 1.27 cm) was attached to the extruder, and the extrudate was water-cooled after exiting the die. Extrusion conditions were described in detail elsewhere.[3]

Sample preparation and fungal decay testing

Side-matched specimens (nominal dimensions: 1.6 mm thickness, 6 mm width, 46 mm length) of WPC and yellow-poplar were cut with the largest specimen dimension coincident with the extruded direction (for WPC) or longitudinal axis (for yellow-poplar). After cutting, all specimens were conditioned to a constant weight at 24°C and 50% relative humidity and weighed to the nearest 0.0001 g. A white-rot fungus, *Trametes versicolor* (USDA Forest Products Laboratory isolate M697), and a brown-rot fungus, *Gloeophyllum trabeum* (USDA Forest Products Laboratory isolate M617), were maintained in Petri dishes on a medium that contained 20 g of malt extract and 15 g of agar (both from Becton, Dickinson and Company, Sparks, MD) per 1 L of water. Freshly prepared agar plates were inoculated with a 1-cm diameter plug of either *T. versicolor* or *G. trabeum*, taken from the edge of an actively growing colony, and incubated at 25°C until the plates were sufficiently covered with mycelium. The conditioned and weighed WPC and yellow-poplar specimens were wrapped with aluminum foil and sterilized in an autoclave at 121°C for 30 min. After cooling, one specimen was placed directly onto the mycelium in each plate to promote moisture uptake of WPC from the agar. Controls were placed on agar plates without the addition of fungal inoculum. For yellow-poplar, only *T. versicolor* was used because, generally, hardwoods are preferentially degraded by white-rot fungi. All plates were sealed with parafilm and incubated at 25°C. Five samples and five side-matched controls of each material were incubated for 24 days with each fungal strain, and six samples and six side-matched controls of each material were incubated for 77 days per fungal strain. Following incubation, samples and controls were recovered from the plates, adhering mycelium was carefully removed from the samples, and all specimens were weighed to the nearest 0.0001 g. The specimens were then placed in a laminar flow cabinet for 30 min to dry the condensation apparent on their surfaces, conditioned to constant weight at 24°C and 50% relative humidity, and weighed to the nearest 0.0001 g. During conditioning, thick glass slides were placed on top of the WPC specimens that were periodically turned to prevent warping. Weight loss (WL) of all specimens was determined as the difference in weight preceding fungal inoculation and following incubation and reequilibration. For WPC, weight loss was calculated as a percentage of the wood filler weight (Table I), assuming that the polyethylene matrix and additives were not degraded.

Statistical analysis

A paired t-test was used to determine if weight losses of fungal-treated samples were significant. Because

TABLE I
Weight loss of WPC Formulations #7 (Wood/HDPE/Additives = 70:24:6) and #3 (Wood/HDPE/Additives = 49:45:6) and Yellow-Poplar after 24 and 77 Days' Incubation with Two Wood Decay Fungi (Standard Deviation in Parentheses)

Material	Treatment	Replicates	Incubation (days)	Weight loss (%)	*P* value
WPC #7	*T. versicolor*	5	24	0.72 (0.47)	0.003
	Control	5		−0.68 (0.07)	
	T. versicolor	6	77	21.03 (3.48)	<0.001
	Control	6		−0.54 (0.06)	
	G. trabeum	5	24	−0.72 (0.28)	Not applicable
	Control	5		−0.79 (0.09)	
	G. trabeum	6	77	7.81 (4.50)	0.005
	Control	6		−0.87 (0.12)	
WPC #3	*T. versicolor*	5	24	−0.11 (0.13)	0.005
	Control	5		−0.52 (0.06)	
	T. versicolor	6	77	18.88 (2.58)	<0.001
	Control	6		−0.51 (0.21)	
	G. trabeum	5	24	−0.56 (0.07)	Not applicable
	Control	5		−0.62 (0.19)	
	G. trabeum	6	77	0.50 (1.23)	0.036
	Control	6		−0.59 (0.14)	
Yellow-poplar	*T. versicolor*	5	24	20.89 (1.01)	<0.001
	Control	5		−1.76 (0.45)	
	T. versicolor	6	77	74.34 (12.00)	<0.001
	Control	6		−1.78 (0.64)	

Weight loss of WPC was based on the wood fraction of the formulation. Samples and controls were significantly different, except for samples treated with *G. trabeum*, incubated for 24 days, and controls.

data obtained for WPC 3, incubated with *G. trabeum* for 77 days, were not normally distributed, the Wilcoxon signed-rank test was used instead in this particular case. Data analysis was conducted using Minitab (version 14).

Dynamic mechanical analysis

Specimens for DMA were dried in a vacuum oven at room temperature until a constant sample weight was obtained. Dynamic mechanical analysis was conducted in dual cantilever mode in a Rheometrics RSA II solids analyzer (Piscataway, NJ). Initially, dynamic strain sweep tests from 10^{-4} to 10^{-3} were run at −50°C, 25°C, and 100°C to ensure linearity throughout the test. Dynamic strain sweep tests were then conducted at 25°C and 1 rad/s (0.159 Hz) with a strain of 10^{-4} to determine possible losses in storage (E') and loss (E'') moduli of the samples from fungal activity. Dynamic temperature scans from −50°C to 100°C were conducted at sequential frequencies of 0.1, 1, and 10 Hz and a strain of 10^{-4} on selected specimens. In all experiments, the heating rate was 2°C/min, and the soak time was 1 min.

The activation energy for the α-transition of WPC was calculated using the Arrhenius equation:[25]

$$k = A_e \exp\left[-\frac{E_a}{RT}\right] \quad (1)$$

where k is the rate constant or test frequency; A_e is the frequency factor; R is the ideal gas constant, 8.314 J/(mol K); T is the temperature (K); and E_a is the activation energy. The peak temperatures of E'' at different frequencies for WPC 7 and WPC 3 were determined using software (RSI Orchestrator, version V6.5.5, Rheometric Scientific, Piscataway, NJ).

Scanning electron microscopy

For scanning electron microscopy, WPC specimens were either freeze-fractured under liquid nitrogen or cut into small sections using a razor blade, then mounted onto stubs and gold-coated in a sputter coater (Technics Hummer V, Anatech, San Jose, CA). The specimens were examined with a Hitachi S-570 electron microscope (Hitachi Scientific Instruments, Tokyo, Japan), and pictures were acquired using a digital camera (Quartz Imaging Corporation, Vancouver, British Columbia, Canada) and imaging software (Quartz PCI—Image Management System, Vancouver, British Columbia, Canada).

RESULTS AND DISCUSSION

Weight loss and moisture content of WPC and yellow-poplar

Calculation of weight loss was based on wood filler because this represents the predominant fungal food

source in the WPC formulations. The biodegradability of high-molecular-weight PE is very limited.[26,27] Once oxygen is introduced into the PE chain and molecular weight is lowered because of photooxidation, the resulting low-molecular-weight material becomes susceptible to biodegradation.[28] In our experiments, some thermal changes may have occurred during autoclaving of the specimens, but it is likely that it was not enough to considerably accelerate the biodegradation rate;[29] in addition, the polyethylene used in this study may have contained some commercial photostabilizers.

To the best of our knowledge, there is only one publication about PE degradation by white-rot fungi,[30] and there is no published information on PE degradation by brown-rot fungi. The white-rot fungi *Phanerochaete crysosporium*, *T. versicolor,* and one unidentified fungal isolate degraded high-molecular-weight PE membranes under nitrogen- or carbon-limited culture conditions.[30] Further research on the decay susceptibility of PE and other types of plastics to wood decay fungi under a variety of environmental conditions is required.

In addition to the wood filler, two of the additives included in our formulations are degradable by fungi: ethylene bis-stearamide wax and zinc stearate.[31,32] It is unlikely that phenolic resin and methyl diisocyanate can be used as food sources by fungi. Future investigations to evaluate the contribution of various additives to the fungal decay susceptibility of WPC are pending. Additives are incorporated into formulations in only small amounts but may play an important role in the biological durability of WPC.

No or extremely low (less than 1%) weight loss was recorded for both WPC formulations after 24 days of incubation with either test fungi (Table I). After 77 days of incubation with *T. versicolor*, weight loss was observed for both formulations—21% for formulation 7 and 19% for formulation 3. By choosing one WPC formulation with a high and one with a low wood filler content, we expected to observe differences between the two formulations in their decay susceptibility and product performance.[3] Minor differences in weight loss after 77 days of incubation between formulations 3 and 7 in our study may be attributed to differences in the degradation rate. Following 77 days of incubation, most of the wood filler in the formulation with the lesser amount of filler (formulation 3) was likely degraded, whereas in formulation 7, probably not all of the wood filler was as yet degraded.

In addition to differences in degradation rate, densification of the wood filler during the extrusion process may play an important role in WPC susceptibility to fungal decay. Densities of both formulations after initial equilibration and prior to fungal inoculation were very similar (1.09 ± 0.02 g/cm^3 for formulation 3 and 1.12 ± 0.02 g/cm^3 for formulation 7), despite the fact that formulation 7 contained 21% more wood filler (by weight) than did formulation 3. Therefore, it is apparent that the wood filler in formulation 7 was densified during extrusion, which, in turn, would likely impart higher fungal decay resistance to formulation 7 than to formulation 3.

Overall, the observed weight losses in this study were much higher than those in previous studies,[3,33] most likely because of the use of very thin, nonstandard-sized samples with a high surface-to-volume ratio.

The weight loss of yellow-poplar incubated with *T. versicolor* was 21% after 24 days and 74% after 77 days of incubation (Table I). These values demonstrate that *T. versicolor* caused significant decay in a nondurable wood species. The noninoculated yellow-poplar controls exhibited no weight loss, which confirms that sterile conditions were maintained during the course of the experiment.

Gloeophyllum trabeum caused weight losses of 8% in formulation 7 and 0.5% in formulation 3 after 77 days incubation. This low weight loss caused by *G. trabeum* may have resulted from this fungus generally being more aggressive in softwoods, whereas *T. versicolor* preferentially degrades hardwoods such as the maple filler contained in our formulations.[34]

The moisture content of WPC and yellow-poplar control specimens was monitored to observe differences in moisture absorption during the testing process (Table II). For WPC, moisture content was calculated as a function of the dry weight of the wood content only. After 24 days of incubation, the moisture content of the yellow-poplar specimens averaged 85%, whereas the moisture contents of formulations 3 and 7 were only 49% and 53%, respectively. However, in both WPC formulations, the minimum moisture threshold for fungal decay, 22%–24%,[35] was surpassed. After a 77-day incubation, no further increase in moisture content was observed in formulations 3 and 7, that is, it appears that the WPC samples were saturated after 24 days. The observed differences in moisture content after initial and final equilibrations were assumed to have resulted from sorption hysteresis.[36]

Dynamic mechanical analysis

Dynamic strain sweep tests

The storage modulus (E') of the yellow-poplar samples decreased following incubation with *T. versicolor* (Fig. 1). After the 77-day incubation, four of six yellow-poplar replicates were so severely degraded that they could not be used in DMA; therefore, the results of DMA for only two replicates are presented. In contrast, after 24 days' incubation with *T. versicolor*, the stiffness of the WPC samples increased slightly (Fig. 1). *Gloeophyllum trabeum* had the same effect as *T. versicolor* on the storage modulus in WPC formulation

TABLE II
Moisture Content of Noninoculated Control Samples for WPC Formulations #3 (Wood/HDPE/Additives = 49:45:6) and #7 (Wood/HDPE/Additives = 70:24:6) and Yellow-Poplar

Material	Incubation (days)	Replicates	Moisture content (%)		
			Initial equilibration	After incubation	Final equilibration
WPC #3	24	10	4 (1.02)	49 (9.71)	6 (0.70)
	77	12	5 (0.70)	42 (7.75)	7 (0.16)
WPC #7	24	10	4 (0.56)	53 (5.32)	5 (0.45)
	77	12	5 (0.29)	50 (5.17)	6 (0.22)
Yellow-poplar	24	5	3 (0.61)	85 (13.59)	5 (0.19)
	77	6	4 (0.84)	92 (22.36)	6 (0.21)

Moisture content was calculated on a dry-weight basis, of wood content only, and presented following initial equilibration, incubation, and final equilibration (standard deviation in parentheses). Initial and final moisture equilibration occurred at 24°C and 50% relative humidity.

7 but not in formulation 3 (Fig. 2). The results obtained for yellow-poplar in the present study confirmed the observations of McCarthy et al.[18] and Birkinshaw et al.,[19] who reported loss in storage modulus in solid wood (*Pinus sylvestris*) as a result of fungal attack by *Coniophora puteana* and *Phanerochaete chrysosporium*.

One interpretation of the E' increase in the inoculated WPC is that the fungal hyphae act as a material reinforcement. Reinforcement effects in composite materials can be evaluated by examining the tan δ (tan δ = E''/E'). The ratio of the tan δ of the decayed samples to that of the controls ($R_{\tan\,\delta} = \tan\,\delta_{decay}/\tan\,\delta_{control}$) allows us to track the development of the fungal hyphae in the wood and composite materials. Essentially, as reinforcement increases, the tan δ of samples should decrease relative to the controls. This behavior was observed for the two WPC formulations after 24 days of incubation with *T. versicolor* (Fig. 3). After 77 days' incubation, little (for formulation 7) or no (for formulation 3) further decrease in $R_{\tan\,\delta}$ of the composites was observed. Using scanning electron microscopy, we were able to confirm that fungal hyphae were present in the wood–plastic interface after only 24 days of incubation with either of the two decay fungi (Fig. 4). This observation corroborates the interpretation that fungal hyphae may act as reinforcement in the voids between the wood filler and the polymer matrix.

The loss modulus (E'') was decreased in yellow-poplar specimens treated with *T. versicolor* after 24 days of incubation, but none of the WPC specimens incubated with the same fungus experienced a decrease in E'' until there had been 77 days of incubation (Fig. 1). This result is not surprising considering that fungal colonization and decay in WPC are expected to proceed more slowly than in solid wood. If this decrease in E'' actually reflects a change in the wood component, it appears that an incubation lasting 77 days was required for *T. versicolor* to colonize

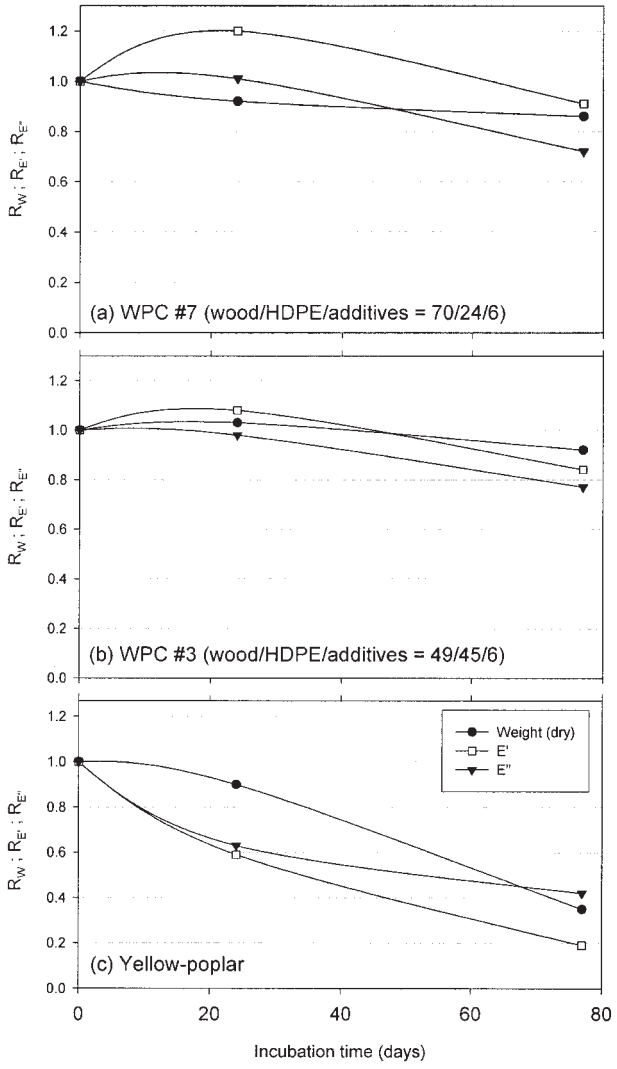

Figure 1 Sensitivity plots (property ratios of samples to controls) for (a) WPC 7, (b) WPC 3, and (c) yellow-poplar following inoculation with *T. versicolor*. Dry weight based on total sample. Ratio of 1 at time of inoculation assumes that autoclaving of specimens had no effect on dry weight, E', and E''. All data were collected in dynamic strain sweep tests at 25°C and 1 rad/s (0.159 Hz), with a strain of 10^{-4}.

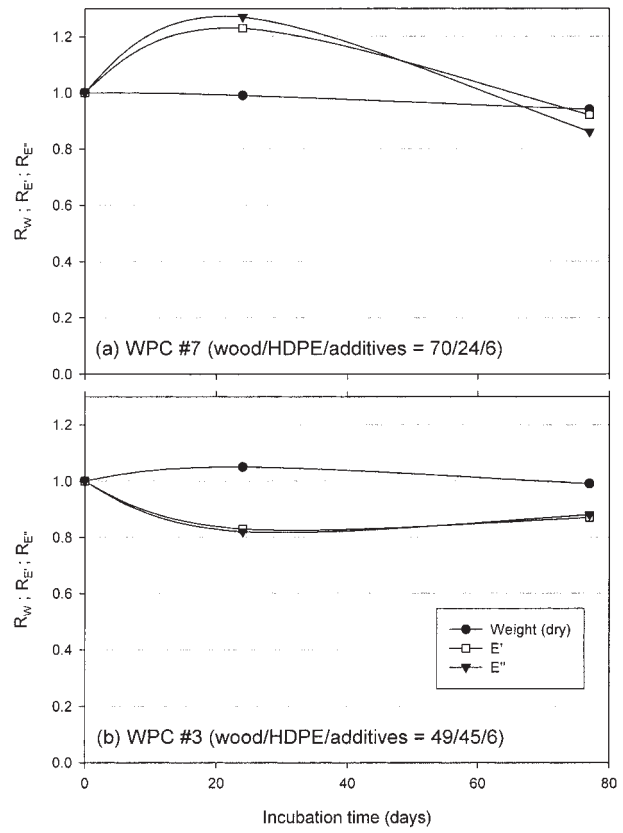

Figure 2 Sensitivity plots (property ratios of samples to controls) for (a) WPC 7 and (b) WPC 3 following inoculation with *G. trabeum*. Dry weight based on total sample. Ratio of 1 at time of inoculation assumes that autoclaving of specimens had no effect on weight, E', and E''. All data were collected in dynamic strain sweep tests at 25°C and 1 rad/s (0.159 Hz), with a strain of 10^{-4}.

the material sufficiently and to degrade the structural cell wall components of wood. The effect of *G. trabeum* on the E'' of the two formulations was variable (Fig. 2); in formulation 3 the loss modulus of the samples was decreased relative to the controls, whereas it was increased in formulation 7.

Comparison of the property ratios of samples to controls for the two WPC formulations and for yellow-poplar allowed us to determine which of the three tested properties (weight, E', and E'') was most sensitive to tracking fungal decay in the material. It appears that for yellow-poplar, storage modulus or stiffness was a more sensitive indicator of fungal decay than was weight loss, whereas weight loss was more suited to evaluating fungal decay in WPC. It should be stressed that the results obtained in our experiments, as in all standard agar or soil block tests, were influenced by a combined effect of fungal activity and moisture. We previously determined that long-term incubation of WPC on agar per se may cause significant loss in stiffness and strength.[33]

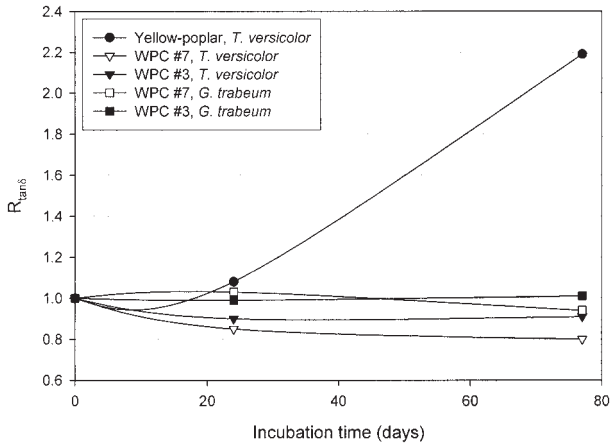

Figure 3 Ratio of tan δ samples to tan δ controls for yellow-poplar, WPC 7 (wood/HDPE/additives = 70:24:6), and WPC 3 (wood/HDPE/additives = 49:45:6) following inoculation with decay fungi. Ratio of 1 at time of inoculation assumes that autoclaving of specimens had no effect on E' and E''. All data were collected in dynamic strain sweep tests at 25°C and 1 rad/s (0.159 Hz), with a strain of 10^{-4}.

Dynamic temperature scans

Dynamic mechanical analysis may facilitate observations about structural changes occurring in wood and WPC because of fungal colonization of the material. Figure 5 presents the temperature dependence of E' and E'' of a formulation 7 sample after 77 days of incubation with *T. versicolor* at three frequencies (0.1, 1, and 10 Hz),

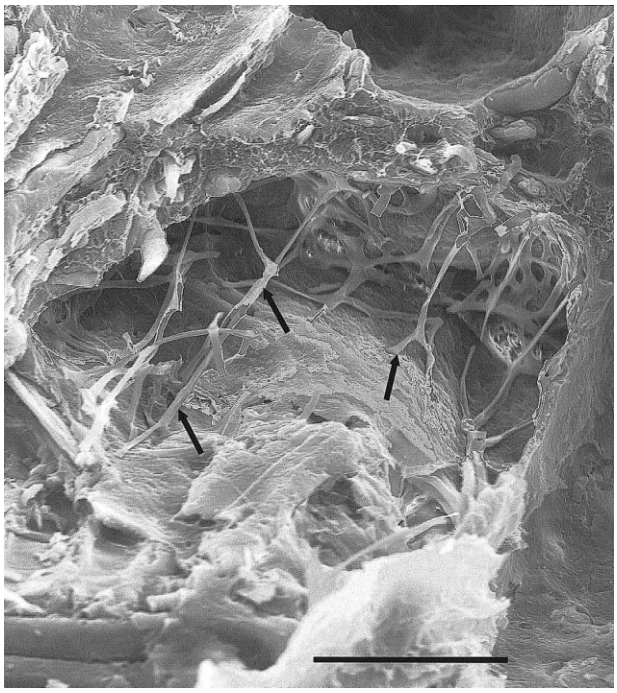

Figure 4 Reinforcement effect of fungal hyphae of *T. versicolor* (arrows) in WPC after 24 days of incubation (formulation 7). Bar represents 40 μm.

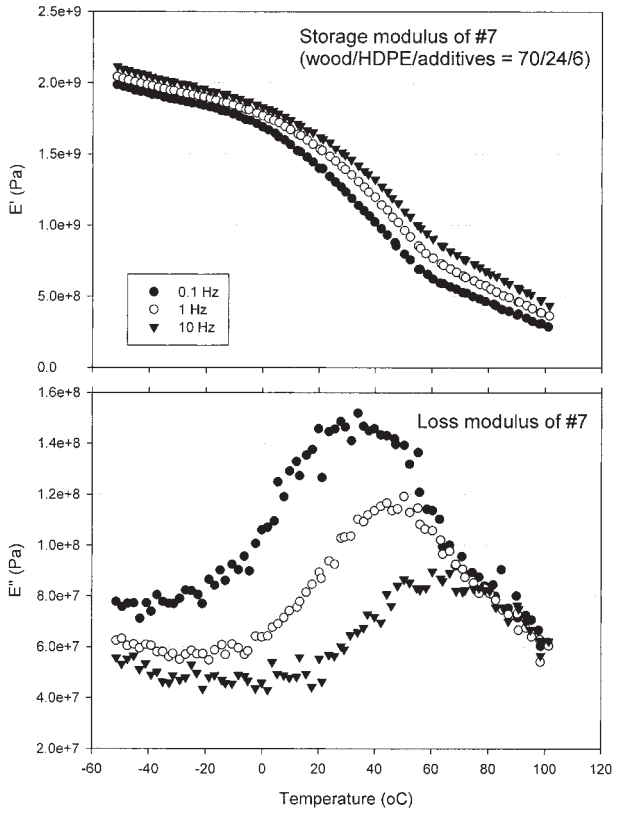

Figure 5 Dynamic temperature scan of a representative WPC sample of formulation 7 following 77 days of incubation with *T. versicolor*.

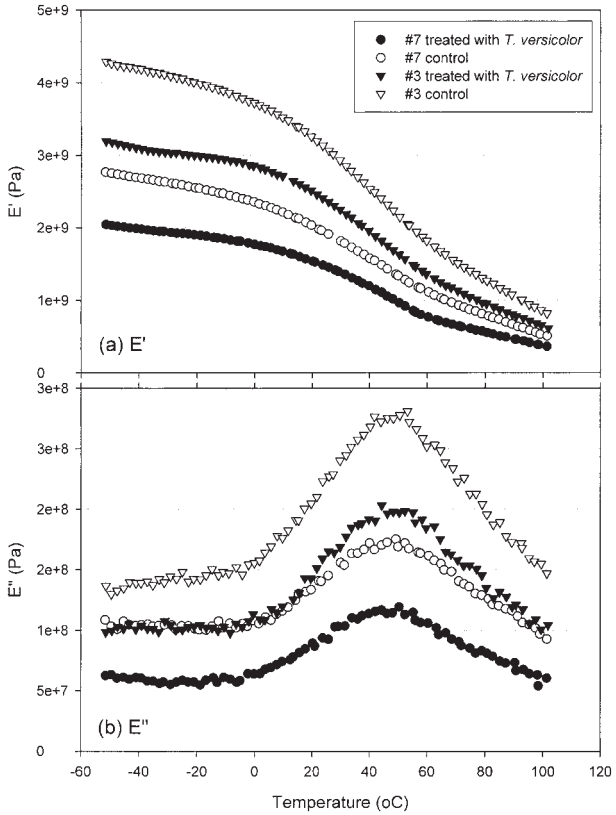

Figure 6 Dynamic temperature scan at 1 Hz frequency of representative samples (incubated with *T. versicolor* for 77 days) and controls of WPC 7 (wood/HDPE/additives = 70:24:6) and WPC 3 (wood/HDPE/additives = 49:45:6).

whereas Figure 6 shows temperature scans for samples and controls at one frequency (1 Hz). With increasing temperature, a drop in E' occurred, yet with increasing frequency, higher values of E' were obtained. A phase transition was noted by a peak in E'' between 30°C and 63°C, depending on the frequency and specimen treatment (Table III). The number of published studies in which transitions in wood-filled HDPE have been identified is limited.[17,37–39] Wang et al.[39] and Balasuriya et al.[38] identified the HDPE γ-transition at −115°C in wood-filled HDPE. The peak temperature of the loss modulus in our spectra represents the α-transition of polyethylene.[23] Simonsen and Rials,[37] who investigated blends of recycled plastics (HDPE and polystyrene) and recycled wood fiber, identified the α-transition of polyethylene at 55°C. Balasuriya et al.[38] and Behzad et al.[17] reported that the α-transition of HDPE shifted to a higher temperature with increasing wood content.

Activation energies for the α-transition in representative WPC samples and controls were calculated using Arrhenius plots (Fig. 7). Activation energy is defined as the energy required to facilitate a reaction between two molecules or the energy required to cause a molecule of a liquid or chain segment of a polymer to jump from its present position to a nearby hole.[16] In general, activation energies obtained for the α-transition in our WPC formulations were comparable to those reported in the literature for various polyethylenes and polyethylene-based composites.[40–42] For composites, a high activation energy is associated with a large degree of interactions between the polymer matrix and the filler.[16] Average activation energy for the α-transition of the formulation 7 samples, inoculated with *T. versicolor* and incubated for 77 days, was 148.9 kJ/mol (n = 3), or 19% higher than that of their controls (120.5 kJ/mol; Fig. 8). The difference in activation energy of formulation 3 samples

TABLE III
Peak Temperatures (°C) of E″ at Three Frequencies for Representative Specimens of WPC #7 (Wood/HDPE/Additives = 70:24:6) and #3 (Wood/HDPE/Additives = 49:45:6)

Frequency (Hz)	#7 Sample	#7 Control	#3 Sample	#3 Control
0.1	33.9	31.6	29.8	29.7
1.0	44.3	46.2	50.4	48.3
10.0	56.0	60.6	58.3	62.6

Samples were inoculated with *T. versicolor;* controls were placed on agar. Incubation time was 77 days.

incubated with *T. versicolor* and their controls was 15% (127.2 kJ/mol versus 107.8 kJ/mol; $n = 3$). These results corroborate the conclusion that fungal hyphae in WPC may improve the interfacial adhesion and stiffness of the material. It is likely that with a higher weight loss in WPC, the observed improvement in composite reinforcement because of fungal colonization would be eliminated or reversed.

CONCLUSIONS

Dynamic mechanical analysis facilitated the investigation of the effects of wood decay fungi on WPC and yellow-poplar. An overall increase in stiffness (storage modulus) of fungal-treated WPC was observed following 24 days of incubation, which may have been caused by hyphal reinforcement of the material and improved interfacial adhesion. This result was supported by the observation that a higher activation energy was required for the α-transition in samples incubated with *T. versicolor* as compared to untreated controls. Stiffness is a more sensitive indicator of fungal decay than is weight loss for a degradable wood species such as yellow-poplar but not for WPC. Further research is required to characterize material changes occurring in WPC after long-term exposure to wood decay fungi.

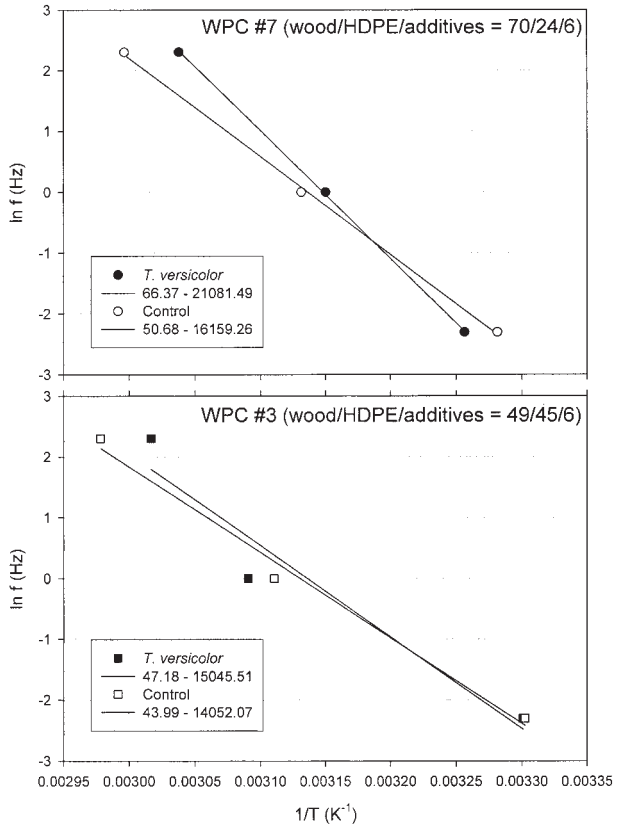

Figure 7 Arrhenius plots for activation energy calculation of α-transition in WPC.

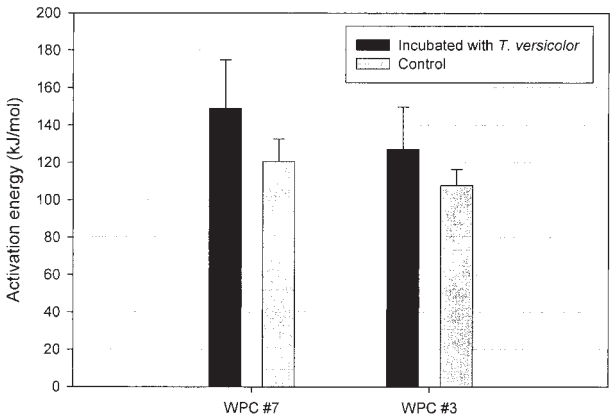

Figure 8 Activation energies for α-transition in WPC 3 (wood/HDPE/additives = 49:45:6) and WPC 7 (wood/HDPE/additives = 70:24:6) incubated with *T. versicolor* and their side-matched controls. Data were collected in frequency–temperature scans performed from −50°C to 100°C at simultaneous frequencies of 0.1, 1, and 10 Hz. Each bar represents the average of three values for the activation energy obtained in individual frequency–temperature scans.

The authors thank the USDA Forest Products Laboratory in Madison, Wisconsin, for donating the fungal isolates used in this study. The authors also gratefully acknowledge advice and help from David Dostal and Chris Hunt; Drs. Tieqi Li, David Harper, and Richard Alldredge; and the Electron Microscopy Center at Washington State University.

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