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Evaluation of the Interfacial Compatibility in Wood Flour/Polypropylene Composites with the Dielectric Approach

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ABSTRACT: To clarify the interaction between the wood and polymer in wood flour/polymer composites, the dielectric constant and dielectric loss factor values were measured for poplar (*Populus tomentasa* Carr.) wood flour/polypropylene (PP) composites with different wood contents. The dielectric relaxation strength, distribution of relaxation time, and activation thermodynamic quantities of the dielectric relaxation caused by the reorientation of the methylol groups (CH_2OH) in the amorphous region of the wood cell wall were then calculated. The results show that the dielectric relaxation strength changed very little below a wood content of 40% and began to increase above that value; this was due to the strong hindrance of PP to the reorientation of methylol groups and, therefore, suggests a close interaction between the wood and PP below a wood content of 40%. The low distribution coefficient of the relaxation time at extremely low temperatures below a 40% wood content was also found; this indicated that some groups in the wood could not move because of the influence of PP. The apparent activation energy increased with wood contents below 40% and then decreased; this further confirmed the optimal interfacial compatibility at a 40% wood content in the wood flour/PP composites in the absence of additives. This result was consistent with the results we obtained by a stress-relaxation approach. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1520–1526, 2013

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INTRODUCTION

Wood flour/polymer composites, as the dominant type of wood/plastic composites, has been used in a variety of applications, including construction, auto parts, packaging, traffic, storage, decorating materials, and daily appliances. However, many researches[1–6] have found that the properties of wood flour/polymer composites greatly depend on the percentages of their constituents and the compatibility between them. Some investigators[4,7–10] have pointed out that the mechanical properties of the composites are low at extremely high or low wood contents, and there is an optimal wood percentage needed to provide the best mechanical properties of the composites. The interfacial compatibility between polar wood flour and a nonpolar polymer has always been the focus of wood flour/polymer studies. A good compatibility usually corresponds to higher mechanical properties in the composites. To investigate the compatibility between wood and polymers, various methods have been applied; these have included microbond and fragmentation testing,[11] single-fiber composites,[12] the fiber pullout method,[13] dynamic mechanical analysis,[14–16] scanning electron microscopy,[17,18] environmental scanning electron microscopy,[19] differential scanning calorimetry,[20] Fourier transform infrared spectroscopy,[21,22] wide-angle X-ray diffraction,[23,24] and electron spectroscopy for chemical analysis.[25,26] These methods can provide some information on the compatibility of the interface but still cannot quantitatively evaluate the interaction between wood flour and the polymer. Recently, we tried to calculate the apparent activation energy (ΔE) of wood flour/polypropylene (PP) composites with various wood contents and different loading levels of coupling agents on the basis of the stress-relaxation behavior of the composites.[9,10] We found that the highest ΔE of the composites without coupling agents appeared at a wood content of 40%; this suggested that the best interfacial compatibility between wood and PP occurred at a 40% wood content with the conditions in this study. Moreover, we found that with increasing loading level of the coupling agents, ΔE increased at first and then decreased gradually. The optimal loading of coupling agent corresponding to the highest ΔE value was related to the wood content and the type of coupling agent. The optimal loading level for maleic anhydride grafted polypropylene (MAPP) was 2% at wood contents of both 50 and 60%, whereas for silane, the optimal loading levels were 1.5 and 2%, respectively, at wood contents of 50 and 60% within the experimental conditions used. Therefore, the interfacial compatibility in the wood flour/polymer composites was indicated.

In this study, we examined another method, the dielectric method, to provide another possibility of quantitatively evaluating the interfacial compatibility. Wood is a dielectric in a relatively low moisture content range. In the oven-dry state, the methylol groups in the amorphous region of the wood cell wall will reorient in an alternating electric field; this causes a dielectric relaxation process in a certain temperature and frequency range.[27,28] Therefore, the dielectric method has been applied to investigate the interaction between wood and adsorbed water and some other modifying agents.[22,29–37] On the basis of the dielectric properties of this material, the activation thermodynamic quantities, including the activation free energy (ΔG), activation enthalpy (ΔH), and activation entropy (ΔS), can be obtained to indicate the energy barrier overcome by the polar groups in wood flour during the reorientation process on the basis of Eyring's absolute rate reaction theory. In a previous study, Wang et al.[38] studied the dielectric properties of Simon poplar wood flour/PP composites with 50–100% wood contents in the oven-dry state and observed an obvious relaxation process based on the reorientation of methylol groups in the amorphous region of the wood cell wall. The dielectric relaxation strength and the relaxation time of the composites were calculated. However, the dielectric properties of the composites at low wood contents were not covered in this previous study, and also, the thermodynamic quantities were not provided to indicate the interfacial compatibility between the wood and PP.

Therefore, in this study, we measured the dielectric properties of wood flour/PP composites with various wood contents (0–70%), and thereafter, the Cole–Cole plots were drawn, and the thermodynamic quantities were calculated. The results were compared with those obtained by the stress-relaxation method to check the applicability of this method.

EXPERIMENTAL

Poplar (*Populus tomentasa* Carr.) wood flour, with a size that passed a 100-mesh sieve, and PP (K8303, Sinopec Chemical Products Sales Co., China), with a density of 0.9 g/cm^3, were used as raw materials to prepare wood flour/PP composites. The PP used was injection-molding grade with a melting temperature around 165°C and a melt flow index of 1.5–2.0 g/10 min at 230°C. The panels were prepared by a compression-molding method with dimensions of 270 × 270 × 3 mm^3 and a target density of 1.0 g/cm^3. Wood flour/PP composites without coupling agent were made at different wood contents of 20, 30, 40, 50, 60, and 70%. A pure PP panel was also prepared as a control group. First, wood flour and PP were weighed and then blended in a high-speed mixer. The mixture was oven-dried and then taken out for hand-matting. A hot press (SYSMEN-II, Chinese Academy of Forestry, China) was used to press the mat at 180°C and 4 MPa for 6 min. After hot pressing, the formed mat was pressed at 4 MPa for another 6 min at room temperature in a cold press. Then, we sawed the prepared panels to smaller sized specimens (32 × 32 × 3 mm^3) and sequentially dried them to the oven-dry state.

The dielectric properties of the specimens were measured with a precision impedance analyzer (Agilent 4294A, Agilent Technologies, United States) equipped with plate electrodes 32 mm in diameter and a temperature-controlling system in the oven-dry sate. The temperature and frequency for dielectric measurements ranged from -80 to 20°C and 1 kHz to 1 MHz, respectively. The programmed rate for the decrease in temperature was 1°C/min. The capacitance value (C_p) and the dielectric loss factor (ε'') were directly obtained, and the dielectric constant (ε') was obtained according to eq. (1):

$$\varepsilon' = (t_a C_p) / \left[\pi \left(\frac{d}{2} \right) \varepsilon_0 \right] \tag{1}$$

where t_a is the mean thickness of the specimens, d is the diameter of the electrodes, and ε_0 is the permittivity of the vacuum (8.845×10^{-12} F/m).

RESULTS AND ANALYSIS

Dielectric Properties of the Wood Flour/PP Composites with Different Wood Contents

The temperature and frequency spectrum of ε' and ε'' of the composites with different wood contents in the oven-dry state are compared in Figure 1. Within the measured temperature and frequency region, an obvious dielectric relaxation process was observed, with a peak occurring around 0°C and 5 MHz in the oven-dry state. It decreased with decreasing wood content and finally disappeared in the pure PP sample.

Norimoto[28] measured the dielectric properties of wood in the oven-dry state and found that a dielectric relaxation process appeared in the frequency range around 10^7–10^8 Hz at room temperature; this was considered to be because of the reorientation of methylol groups (CH_2OH) in the amorphous region of the wood cell wall. In wood flour/PP composites, ε'' is mainly dependent on wood flour because PP is a nonpolar material. However, the temperature and frequency range in which the dielectric relaxation process appeared moved to higher temperatures compared with that in wood; this was also observed by Wang et al.[38] This movement was considered to be related to the hindrance from long-chained PP molecules; this inhibited the reorientation of methylol groups. Therefore, with decreasing wood content, the percentage of PP increased correspondingly, and this resulted in a greater hindrance to the reorientation of the methylol groups. Finally, the dielectric process disappeared when the wood content reached zero.

Cole–Cole Plots of the Wood Flour/PP Composites with Various Wood Contents

To further analyze the dielectric properties, Cole and Cole[39] obtained the circumference while plotting ε'' on the ordinate and ε' on the abscissa and applying the angular frequency (ω) as a variable. It is called Debye distribution when the relaxation time in a given material is all the same. However, the wood cell wall consists of different substances, such as cellulose,

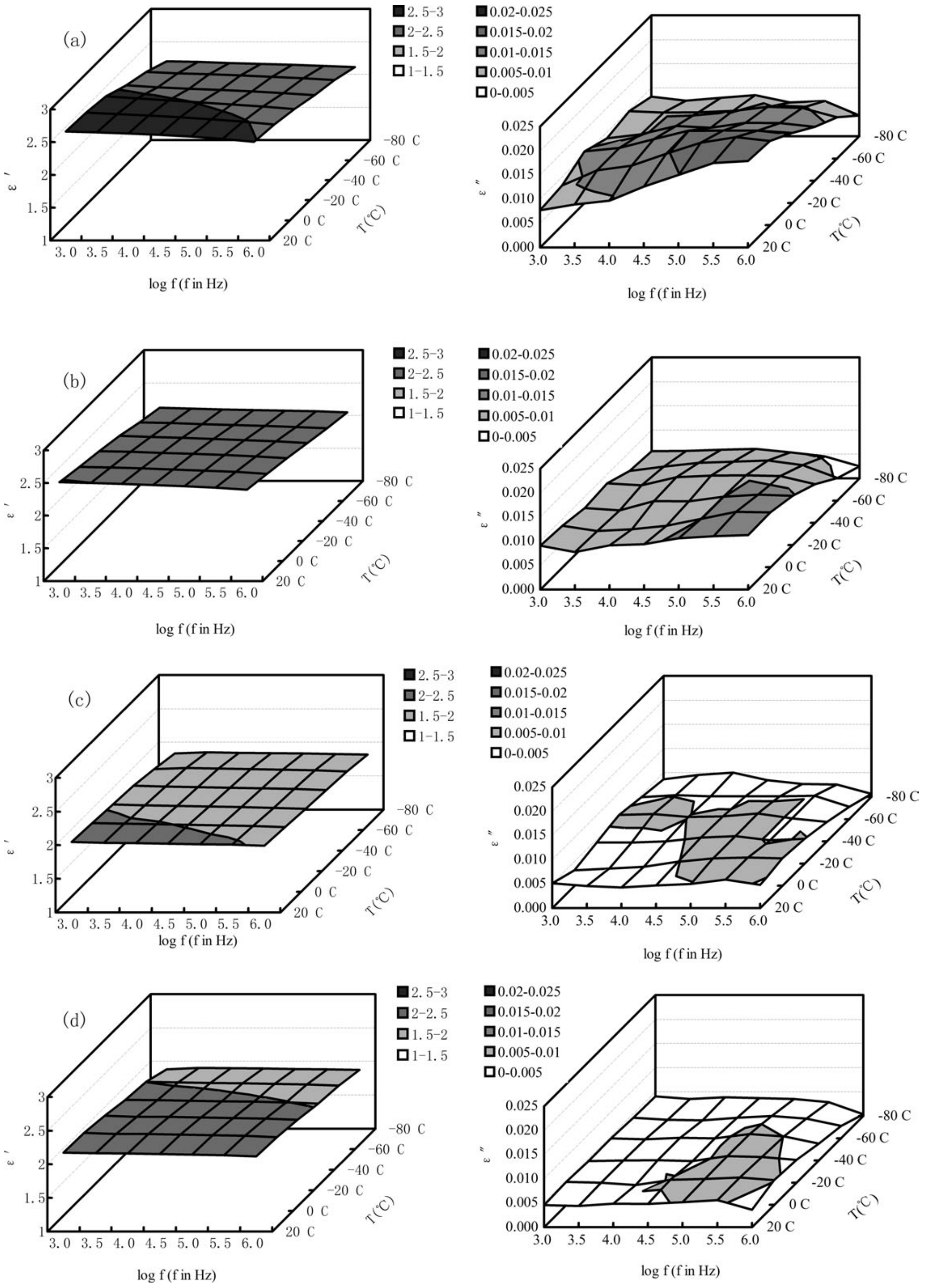

Figure 1. Temperature and frequency spectra of ϵ' and ϵ'' of the wood flour/PP composites with different wood contents: (a) 70, (b) 60, (c) 50, (d) 40, (e) 30, (f) 20, and (g) 0%.

hemicellulose, and lignin, so the relaxation times of wood are distributed around the most probable value.[40] Cole–Cole plots, which can be expressed by eq. (2), are applied to the dielectric data of wood flour/PP composites:

$$\varepsilon^* = \varepsilon_0 + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_m)^{1-\alpha}} \tag{2}$$

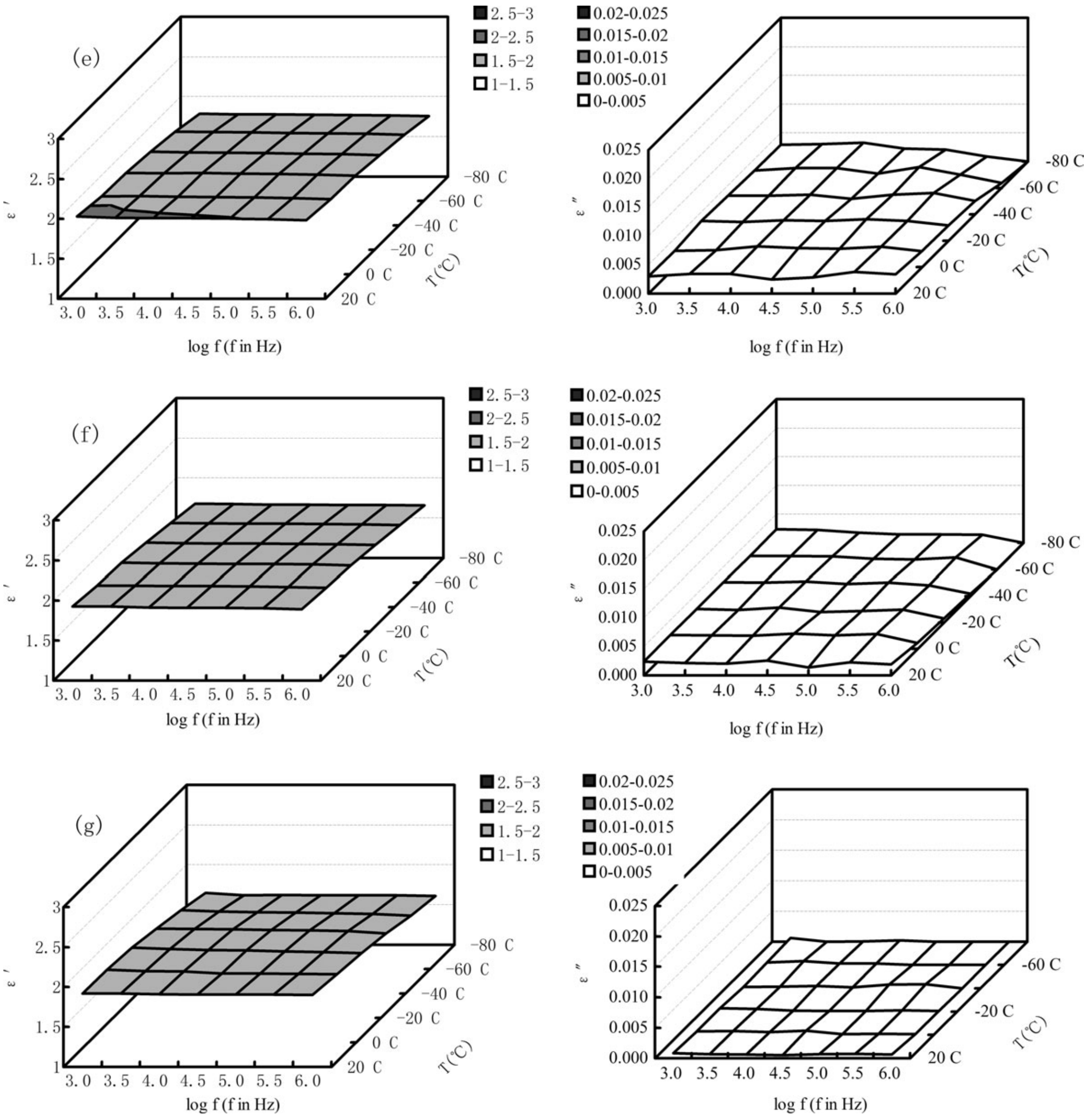

Figure 1. Continued

where ε^* is the complex dielectric constant; ε_s is the static dielectric constant, which corresponds to ε'' at an extremely low frequency; ε_∞ is the optic dielectric constant, which corresponds to the relative ε'' at an extremely high frequency; $\varepsilon_s - \varepsilon_\infty$ is the relaxation strength and represents the magnitude of dielectric relaxation; $\omega = 2\pi f$, where f is the frequency; τ_m is the average relaxation time; and α ($0 \leq \alpha < 1$) is the parameter that characterizes the relaxation time distribution. A high α value suggests a broad relaxation time distribution. When $\alpha = 0$, this equation is reduced to the Debye equation.

Two groups of Cole–Cole plots could be obtained from the dielectric relaxation of the wood flour/PP composites within the measured temperature and frequency region with different wood contents at $-60°C$, as shown in Figure 2. On the basis of these Cole–Cole plots, the relaxation strength ($\varepsilon_s - \varepsilon_\infty$) of the methylol groups in the wood flour/PP composites at different wood contents was obtained, as shown in Figure 3.

Figure 3 shows that the dielectric relaxation strengths all tended to increase with increasing wood content at various

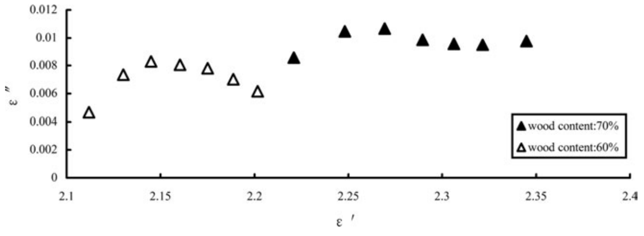

Figure 2. Cole–Cole plots for the wood flour/PP composites with different wood contents at $-60°C$.

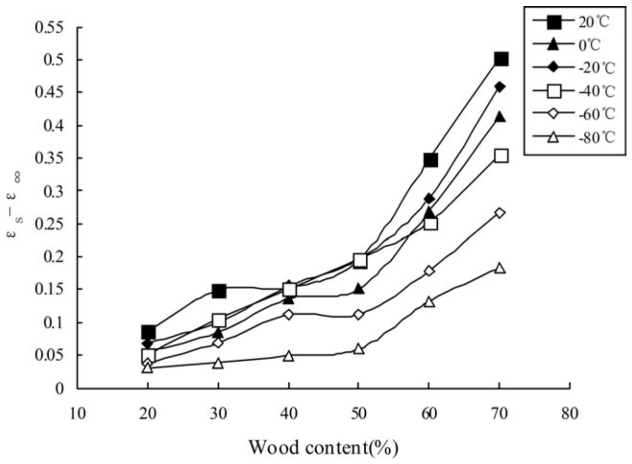

Figure 3. Relaxation strength ($\epsilon_s - \epsilon_\infty$) of the methylol groups in the wood flour/PP composites with various wood contents obtained from Cole–Cole plots at different temperatures.

temperatures. Below a 40% wood content, the relaxation strength changed very little; then, it increased slightly within the 40–50% wood content range. Above a 50% wood content, the relaxation strength increased obviously with increasing wood content. The increase in the relaxation strength with increasing wood content above 50% was also observed by Wang et al.[38] The higher relaxation strength represented more methylol groups participating in the reorientation process. When the wood content was below 50%, the obstacles from the PP molecules were obvious; this resulted in a lower number of reorienting methylol groups. This indicates that the compatibility between wood and PP was good in composites with wood contents of less than 50%.

Temperature also plays an important role in influencing the relaxation process. At low temperatures, the relaxation strength is also low because the molecules or groups always require energy to reorient. Correspondingly, the relaxation times also tend to be low at low temperatures, especially at lower wood contents. As shown in Figure 4, the coefficient α at −80°C was around 0.8 below a 40% wood content, but at wood contents above 40%, it increased rapidly and finally reached a similar level as at other temperatures. We considered this to be caused by the hindrance of PP, which prolonged the reorientation time of the methylol groups at wood contents below 40%.

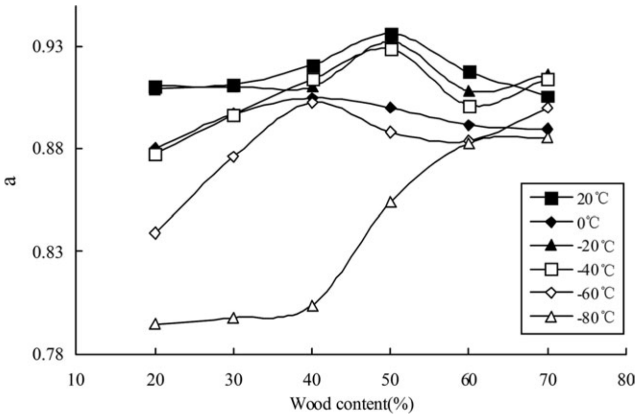

Figure 4. Change in describing the distribution of the relaxation times (a) of the wood flour/PP composites at different wood contents obtained from Cole–Cole plots at various temperatures.

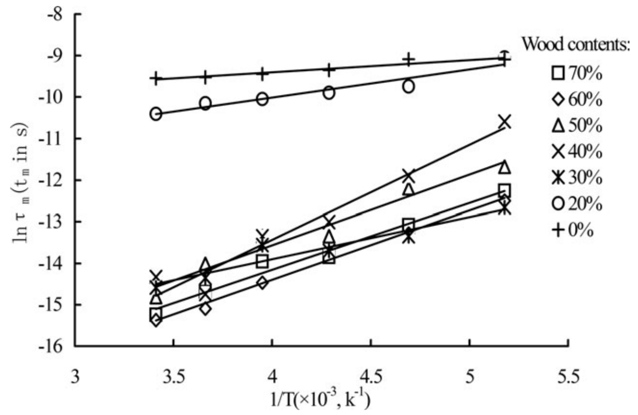

Figure 5. Relationship between the logarithm of the average relaxation time ln τ_m(τ_m in s) and the reciprocal of the absolute temperature ($1/T$) for the wood flour/PP composites.

Activation Thermodynamic Quantities of Samples with Different Wood Contents

The activation energy required for the relaxation of methylol groups in wood was calculated on the basis of the dielectric properties because the relaxation process of wood agrees with Eyring's absolute velocity reaction law, which is shown as follows:

$$\tau = \tau_0 e^{\Delta E/RT} \tag{3}$$

ΔG, ΔH, and ΔS were calculated according to the following equations:[41]

$$\Delta H = \Delta E - RT \tag{4}$$

$$1/\tau_m = (kT/h)e^{-\Delta G/GT} \tag{5}$$

$$T\Delta S = \Delta H - \Delta G \tag{6}$$

where τ is relaxation time, τ_0 is the constant, R is the gas constant, T is the Kelvin temperature, k is Bolzmann constant, h is Planck constant and ΔE is the value of ΔE during relaxation. The generalized relaxation time (τ_m) at different temperatures was calculated by $\tau_m = 1/(2\pi f_m)$, where f_m is the frequency at which the peak of ε'' appears. According to the relationship between ln τ_m and $1/T$, the values of ΔE were calculated with the slope of the plots.

The curves of ln τ_m versus $1/T$ of the wood flour/PP composites with different wood contents are given in Figure 5. All of the R^2 values of regression curves were greater than 0.9; this suggested a good linearity between ln τ_m and $1/T$ at all of the wood contents used in this study. The obtained ΔE values are shown in Figure 6. As shown in Figure 6, the ΔE values of the wood

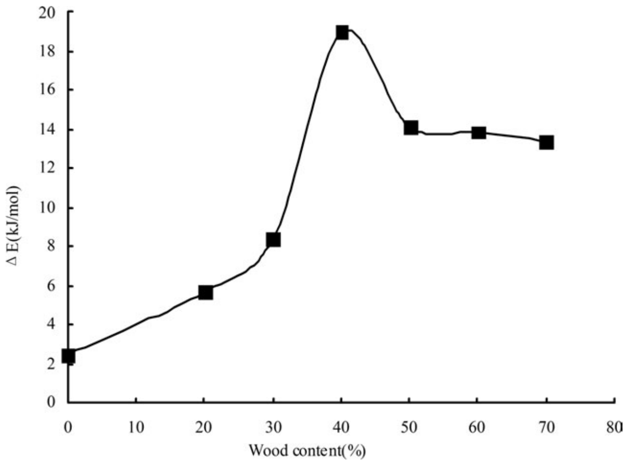

Figure 6. Δ*E* values of the wood flour/PP composites with various wood contents.

flour/PP composites increased first and then decreased with increasing wood content and achieved a maximum at a wood content of 40%. This was consistent with results obtained by the stress-relaxation approach.[9] The bending modulus of rupture and modulus of elasticity of the wood flour/PP composites at a 40% wood content also reached their maximum values according to our previous study.[9]

Table I shows that ΔH and ΔS, the same as ΔE, all tended to increase first and then decrease; in contrast, ΔG tended to decrease first and then increase. In the case of the dielectric relaxation process, ΔS is physically defined as the difference between the entropy of methylol groups (CH_2OH) in the amorphous region of the wood cell wall in the activated state (i.e., during reorientation) and that before reorientation.[32] ΔS (the negative indicates an increase in entropy) increased; this suggested that the wood flour/PP composites were more stable and conversely decreased; this suggested a tendency to be ordered and indicates that the barrier of the dielectric relaxation process decreased, the dielectric relaxation properties deteriorated, and the stability of the wood flour/PP composites was the best at a 40% wood content.

The reorientation hindrance of the methylol groups was closely related to the interfacial compatibility between wood flour and PP. Better interactions between the wood flour and PP corresponded to higher activation energy; namely, more energy would be required to make the methylol groups in the composite reorient. Obviously, the interfacial compatibility between the wood flour and PP reached the best state at a wood content of 40%.

CONCLUSIONS

The dielectric relaxation observed in the wood flour/PP composites, which was based on the reorientation of methylol groups in the amorphous region of the wood cell wall, decreased with decreasing wood contents and disappeared at wood content of 0%. According to the calculated results of the relaxation strength and activation energy, the wood content of 40% was a critical point at which the best interfacial compatibility between the wood flour and PP could be achieved. The results agreed well with those obtained by the stress-relaxation approach in our previous study. Therefore, it could also be used as a tool to quantitatively evaluate the compatibility between wood flour and a polymer in wood flour/polymer composites. The effect of a coupling agent on the dielectric relaxation will also be studied in further research.

Table I. ΔG, ΔH, and ΔS Values of the Dielectric Relaxation of the Wood Flour/PP Composites at −20°C

Wood content (%)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J mol^{-1} k^{-1})
20	3.54	38.40	−137.70
30	6.30	33.11	−105.91
40	16.86	33.55	−65.93
50	12.03	33.55	−85.03
60	11.76	31.20	−76.83
70	11.26	32.08	−82.23

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