Understanding the Viscoelastic Properties of Extruded Polypropylene Wood Plastic Composites

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ABSTRACT: The main goal of this study was to analyze the effect of process additives, that is, maleated polypropylene (MAPP), and a nucleating agent on the viscoelastic properties of different types of extruded polypropylene (PP) wood plastic composites manufactured from either a PP homopolymer, a high crystallinity PP, or a PP impact copolymer using dynamic mechanical thermal analysis. The wood plastic composites were manufactured using 60% pine wood flour and 40% PP on a Davis-Standard Woodtruder™. Dynamic mechanical thermal properties, polymer damping peaks (tan δ), storage modulus (E'), and loss modulus (E'') were measured using a dynamic mechanical thermal analyzer. To analyze the effect of the frequency on the dynamic mechanical properties of the various composites, DMA tests were performed over a temperature range of -20 to $100°C$, at four different frequencies (1, 5, 10, and 25 Hz) and at a heating rate of $5°C/min$. From these results, the activation energy of the various composites was measured using an Arrhenius relationship to investigate the effect of MAPP and the nucleating agent on the measurement of the interphase between the wood and plastic of the extruded PP wood plastic composites. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1638–1644, 2003

Key words: additives; activation energy; nucleating agent

INTRODUCTION

Composite materials are created by combining two or more components to achieve desired properties, which could not be obtained with the separate components. The use of reinforcing fillers, which can reduce material costs and improve certain properties, is increasing in thermoplastic polymer composites. Currently, various inorganic materials such as talc, mica, clay, glass fiber, and calcium carbonate are being incorporated into thermoplastic composites.[1]

Nevertheless, agricultural fillers, for example, wood fiber or wood flour, have drawn attention due to their abundant availability, low cost, and renewable nature. In recent years, interest has grown for composites made from wood flour or wood fiber in thermoplastic matrices, particularly for low-cost/high-volume applications. In addition to high specific properties, wood and cellulose fibers offer a number of benefits for wood–thermoplastic composites. These include low hardness, which minimizes abrasion of the equipment during processing, relatively low density compared with composites reinforced by inorganic materials, biodegradability, and low cost on a unit–volume basis.

In spite of the advantages mentioned above, the use of wood flour or wood fibers in thermoplastic composites has been plagued by difficulties in obtaining good dispersion and strong interfacial adhesion because wood flour is hydrophilic and matrix polymers are hydrophobic. Therefore, to improve the mechanical properties of wood flour-reinforced polymers, various coupling agents and nucleating agents have been used in the last few years, especially those based on anhydride, maleated polypropylene (MAPP), and silane as a coupling agent[2,3] or sodium benzoate as a nucleating agent being the most utilized.[4,5] Furthermore, the final product properties are highly dependent on the rheological conditions during the processing. The properties of composite materials are also determined by the characteristics of the polymer matrices themselves, together with reinforcement and the adhesion fiber/matrix interface that depends mainly on voids and the bonding strength at the interface.

Dynamic mechanical analysis over a wide range of temperature and frequencies permits the determination of the viscoelastic behavior of molten polymers and, in particular, the study the glass transition of reinforced composites. The main objective of this study was to analyze the effect of process additives, that is, MAPP, and a nucleating agent on the viscoelastic properties of different types of extruded polypropylene (PP) wood plastic composites manufactured

from a regular PP homopolymer, high-crystalline PP, or a PP impact copolymer using dynamic mechanical thermal analysis.

EXPERIMENTAL

Materials and composite preparation

The extrusion runs utilized the following PP, which were supplied by BP Amoco Chemicals (Naperville, IL):

- High-crystalline PP homopolymer with 2% MAPP (HCPP-M)
- High-crystalline PP homopolymer with a nucleating agent (HCPP-N)
- Regular PP homopolymer with 2% MAPP (RPP-M)
- Regular PP homopolymer with a nucleating agent (RPP-N)
- Random copolymer PP with 2% MAPP (COPP-M)
- Fractional melt-flow rate (MFR) PP homopolymer with 2% MAPP (FMPP-M).

The nucleating agent was sodium benzoate in a concentration of several hundred parts per million. Wood flour made from southern pine ground to 40 mesh was obtained from American Wood Fibers, Inc. (Columbia, MD). The wood plastic composite lumber was manufactured using 60% pine wood flour and 40% PP on a Davis-Standard Woodtruder™. The WPC lumber was made using either a 3/4 × 5.5-in. die or a 5/4 × 5.5-in. die.

Measurements

Dynamic mechanical thermal analysis (DMTA) was conducted on a Model Mk IV DMTA instrument from Rheometrics Scientific. The dual-cantilever bending mode was selected. Samples of dimension 34 × 6 × 3-mm thickness were cut from the wood plastic composite lumber.

Tests were performed over a wide frequency range (1, 5, 10, and 25 Hz) and the temperature programs were run from −20 to 100°C under a controlled sinusoidal strain, at a heating rate of 5°C/min under a flow of liquid nitrogen. An oscillating dynamic strain of 0.01% was used. The viscoelastic properties such as the storage modulus (E'), the mechanical loss factor (E''), and the damping ratio (tan $\delta = E''/E'$) were recorded as a function of the temperature and frequency.

It has been suggested that it is possible to interrelate the temperature at which a relaxation process is observed with the frequency of excitation (f) by the Arrhenius equation[6]:
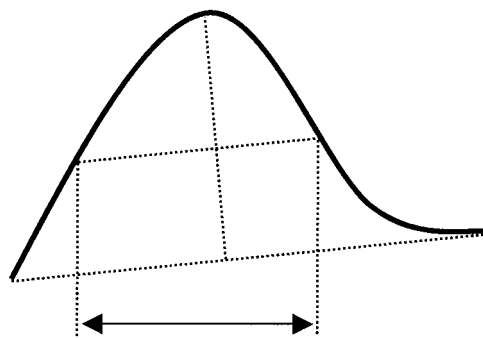

Figure 1 Criteria of definition of the parameter peak width at half-maximum.

$$f = f_0 \exp(-E_a/RT) \tag{1}$$

where f_0 is a constant; f, the frequency of the test; R, the gas constant (8.314 J g^{-1} mol^{-1} K^{-1}); and E_a, the activation energy for the relaxation process. From this Arrhenius equation, the activation energies were also calculated.

The peak width at half-maximum (see Fig. 1 for a scheme of the criteria used to define this parameter) refers to the homogeneity of the amorphous phase, so that a bigger peak width at the half-maximum value implies a higher heterogeneity of the amorphous phase. The DMTA software also calculated the area under the peak.

RESULTS AND DISCUSSION

DMA measurements

To evaluate the effect of the process additives, that is, MAPP, and the nucleating agent on the viscoelastic properties of different types of extruded PP wood plastic composites, the storage modulus (E') as a function of temperature at four frequencies is graphically represented in Figures 2–5. Tables I–III list the storage modulus, tan δ, and glass transition temperatures of the wood–PP composites determined at four different frequencies and 20°C. At room temperature, the high-crystalline PP composites had the highest storage modulus values and glass transition temperatures. With respect to the frequency effect, its influence on the storage modulus is very small. According to the results shown in Tables I–III and Figures 2–5, the storage moduli of high-crystalline PP composites treated with MAPP as a coupling agent were higher than those of other wood–PP composites in the following manner:

HCPP-M > HCPP-N = FMPP-M

> RPP-M > RPP-N > COPP-M

Figure 2 Storage modulus of extruded PP wood plastic composites as a function of temperature at 1 Hz.
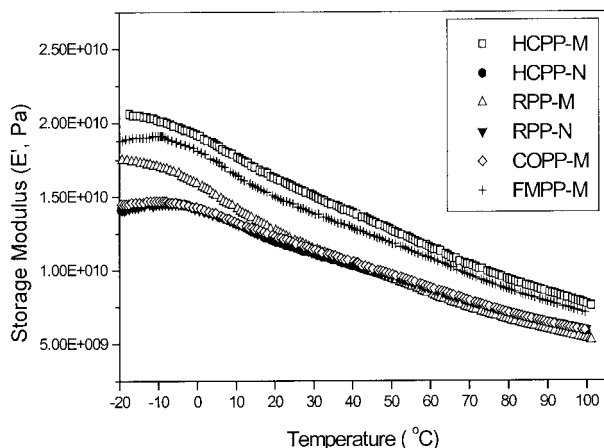

Figure 4 Storage modulus of extruded PP wood plastic composites as a function of temperature at 10 Hz.

As crystallinity and spherulite size increase, the modulus of the wood–PP composites increase, and their strength and deformability decrease.[7]

With respect to the processing additives, the effect of MAPP as a coupling agent on the composite stiffness was larger than that of the nucleating agent on the wood–PP composites. It is generally accepted that the improvement in the strength properties of the composites is achieved through grafting between the wood flour or fiber and MAPP by esterification. Felix and Gatenholm[8] explained the role of MAPP as an adhesion promoter in the following way: The anhydride groups of MAPP react chemically with the hydroxyl groups of the wood flour or fiber to form ester bonds (covalent bonds), whereas nucleating agents increase the number of crystallization sites in a polymer, resulting in an increase in the overall crystallization rate. The enhanced crystallization rate also results in crystallization errors such as intercrystalline links.
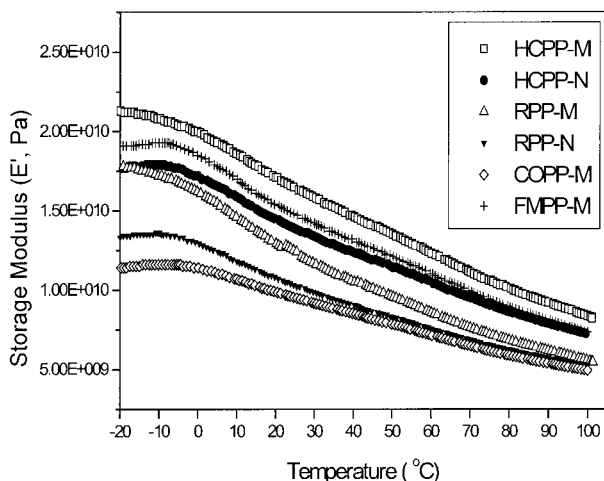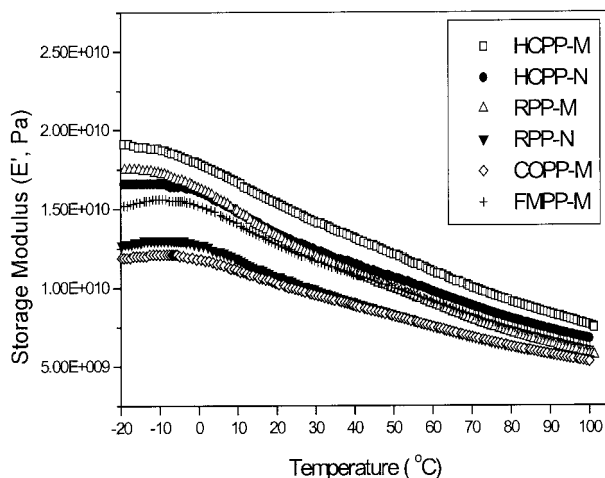
Intercrystalline links are bridges between and within spherulites generated by a PP chain that has one segment crystallized in one spherulite and another segment crystallized in another spherulite or another part of the same spherulite. Thus, a PP chain can link two spherulites together. Nucleating agents, through intercrystalline links and smaller spherulites, improve the impact strength, tensile strength, and clarity of PP.[9] Therefore, nucleating agents have no effect on the interfacial adhesion between wood flour and a polymer. For this reason, we suggest that the MAPP was more effective than was the nucleating agent in improving the interfacial adhesion between the hydrophilic wood flour and hydrophobic PP.

The storage moduli of the impact copolymer PP composites were lower than those of other wood–PP composites because the impact copolymer PP matrix is composed of an ethylene–propylene random copolymer with a high impact strength. In other words, to
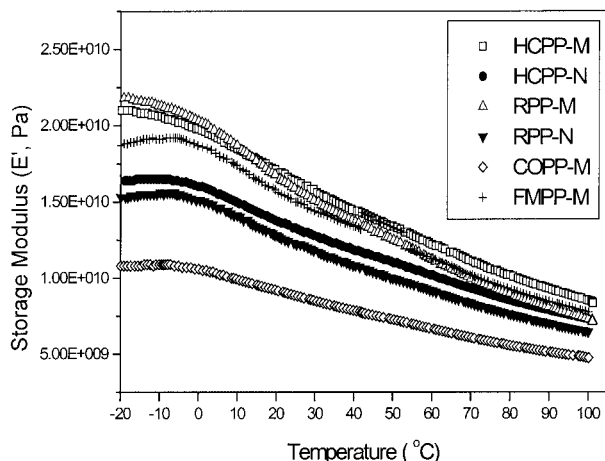

Figure 3 Storage modulus of extruded PP wood plastic composites as a function of temperature at 5 Hz.

Figure 5 Storage modulus of extruded PP wood plastic composites as a function of temperature at 25 Hz.

TABLE I
Storage Modulus of the Materials Investigated at 20°C

Materials	Storage modulus (E', GPa)			
	At 1 Hz	At 5 Hz	At 10 Hz	At 25 Hz
HCPP-M	16.2	17.1	15.4	17.1
HCPP-N	11.9	14.5	13.5	13.8
RPP-M	12.7	12.9	13.2	16.8
RPP-N	12.0	10.8	10.7	12.8
COPP-M	12.3	9.91	10.2	9.22
FMPP-M	15.1	15.4	12.8	15.8

TABLE III
Glass Transition Temperature and Tan δ Values at the Peak of Tangent Curves (Frequency: 10 Hz)

Materials	Glass transition temperature (°C)	Tan δ at the peak
HCPP-M	15.64	0.043
HCPP-N	14.54	0.046
RPP-M	14.82	0.051
RPP-N	13.80	0.048
COPP-M	14.63	0.057
FMPP-M	13.05	0.044

improve the impact strength of PP, we can substitute some part of the side chain of PP for ethylene, which has high toughness as a copolymer and results in relatively lower mechanical properties of the composite such as the strength and modulus.

The effect of the PP type and processing additives on the damping ratio of the wood–PP composites and tan δ as a function of temperature are graphically represented in Figures 6 and 7, and the values are listed in Tables I and II. As shown in these figures, the values of tan δ for the various types of wood–PP composites are ranked as follows:

COPP-M > RPP-M ≥ RPP-N

≫ HCPP-N ≥ HCPP-M = FMPP-M

The peak area under the tan δ curves and peak width at half-maximum of the composites as a function of the PP and processing additives are listed in Table IV. The peak width at half-maximum is a criterion used to indicate interaction between the phases and the homogeneity of the amorphous phase and a higher value implies a better interaction between the phases and a higher heterogeneity of the amorphous phase.[10]

The decrease of the value of tan δ and the increase in the peak width at half-maximum of high-crystalline PP composites compared to regular PP composites can be attributed to the lower mobility of the polymer chains in this composite system. Generally, the value of tan δ (E''/E') describes the flexibility or stiffness of the composites. From the values listed in Table IV, therefore, in the case of the regular PP with a lower

stiffness or modulus, the curve of tan δ is very narrow and does show a clear peak compared with the high-crystalline PP–wood composites. Thus, the results shown in Figures 6 and 7 were in accordance with those of the storage modulus (E') values. According to Table I, on the other hand, the impact copolymer PP composites exhibit considerably higher tan δ values, corresponding to a higher impact strength and toughness, as compared with other types of PP composites.

It is noted that the glass transition temperature (T_g) remains nearly unchanged regardless of processing additives, that is, the coupling agent and nucleating agent in the same composite matrix. On the other hand, the regular PP treated with a coupling agent or nucleating agent gives rise to a displacement of the T_g peak to higher temperatures, as can be observed in Figures 6 and 7. From these results, it can be deduced that the intensity and magnitude of the peak height sensibly changed as a function of the type of PP (high-crystalline or regular type) matrix.

Calculation of the activation energy

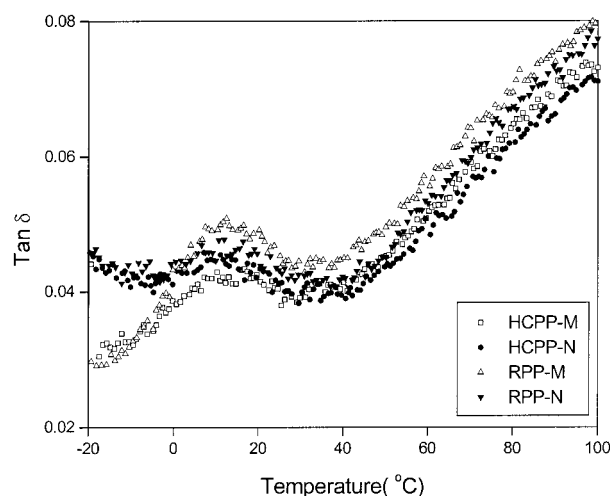To analyze the effect of the frequency on the dynamic mechanical properties of the various composites,

TABLE II
Tan δ Values of the Materials Investigated at 20°C

Materials	Tan δ values			
	At 1 Hz	At 5 Hz	At 10 Hz	At 25 Hz
HCPP-M	0.042	0.046	0.048	0.066
HCPP-N	0.042	0.045	0.053	0.068
RPP-M	0.049	0.049	0.057	0.080
RPP-N	0.046	0.049	0.058	0.075
COPP-M	0.042	0.048	0.056	0.078
FMPP-M	0.042	0.042	0.044	0.053

Figure 6 Tan δ of high crystalline and regular PP wood flour-reinforced composites as a function of temperature at 1 Hz.

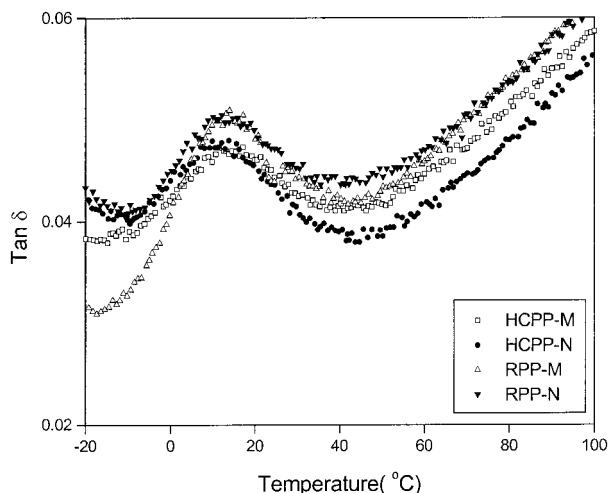**Figure 7** Tan δ of high-crystalline and regular PP wood flour-reinforced composites as a function of temperature at 5 Hz.

Figure 8 Effect of the frequency on DMA spectra of high-crystalline PP composite treated with MAPP.

DMA tests were performed over a temperature range of −20 to 100°C, at four different frequencies (1, 5, 10, and 25 Hz). In Figures 8–10, the temperature dependence of tan δ for crystalline and regular PP composites with MAPP is represented at the four frequencies studied. From these figures, it can be inferred that the effect of the frequency on the peak magnitude does not show a clear tendency, but the relaxation peak temperature is increased by about 3°C when the frequency increases from 1 to 25 Hz. These peaks are also influenced by the frequency used during the test where an increase in the frequency shifts the peaks to higher temperatures.[11] According to the Arrhenius equation, a plot of log f versus $1000/T$ (Fig. 11) should give a straight line with a slope that is proportional to the apparent activation energy for the relaxation process of various types of wood–PP composites.

Calculated activation engeries according to eq. (1) are shown in Figure 12. As shown in Figure 12, the activation energies of high-crystalline PP with MAPP or the nucleating agent were about 373 and 369 kJ/mol, respectively, and those of regular PP with MAPP or the nucleating agent were about 275 and 276 kJ/mol, respectively. The activation energy of the impact

copolymer PP treated with MAPP was about 140 kJ/mol, the lowest value of all the composites. From these data, the activation energies of high-crystalline PP composites were larger than those of the regular PP composites. Also, compared with virgin PP, which has 243 kJ/mol of activation energy,[12] 60% wood flour-reinforced PP composites have much higher activation energies.

Activation energy is described 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, that is, an empty volume of a molecular or chain-segment size in the liquid.[13] Joseph et al.[14] reported that the activation energy values increase with an increase in the fiber content up to 30% except in the case of 10% fiber loading. Similarly among the untreated and treated fiber-reinforced composites, the highest activation en-
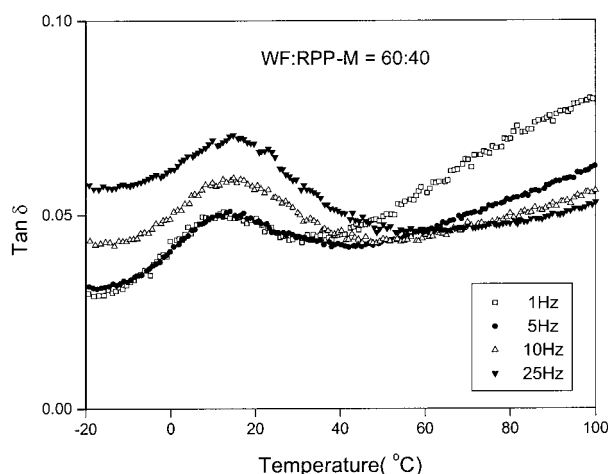
TABLE IV
Area and Width at Half-maximum of Tan δ Peak of High-crystalline and Regular PP Wood Flour-reinforced Composites

Material	Area under the peak		Peak width at half-maximum	
	At 1 Hz	At 5 Hz	At 1 Hz	At 5 Hz
HCPP-M	16.25	42.23	20.95	21.83
HCPP-N	19.34	43.21	19.53	20.52
RPP-M	25.31	66.53	17.53	18.53
RPP-N	30.02	56.43	17.20	16.23

Figure 9 Effect of the frequency on DMA spectra of regular PP composite treated with MAPP.
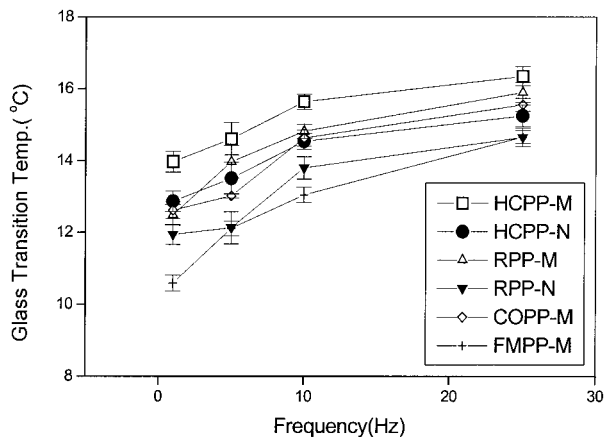
Figure 10 Glass transition temperature of extruded PP wood plastic composites as a function of frequency.

Figure 12 Activation energies of the wood–PP composites.

ergy value is obtained for chemically treated fiber-reinforced composites. It can be seen that the activation energy values are able to indirectly represent the fiber/matrix reinforcement.

Given that strong interactions between the fiber and polymer can substantially alter the mobility of polymer chains within the interphase, this technique can provide insight into the mechanics of interfacial interactions and the relative volume of the interphase (Rials et al.[15]). In other words, more energy is required to move a molecule between two materials when composites have a higher activation energy. Consequently, the composite having a high activation energy indicates good dispersion or adhesion between interphase developments of the polymer and the filler, which results in good mechanical properties under similar conditions.

CONCLUSIONS

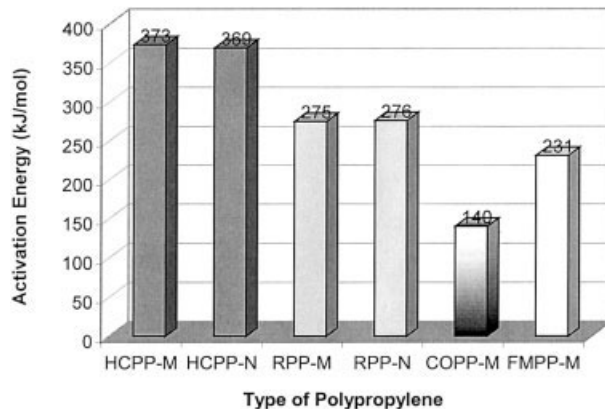This study was designed and performed to analyze the effect of process additives on the viscoelastic prop-

erties of different types of extruded PP wood plastic composites by using dynamic mechanical thermal analysis. In addition, the activation energy of the various composites was calculated from these results.

The storage moduli of high-crystalline PP composites treated with MAPP as a coupling agent were higher than those of other wood–PP composites in the following manner:

HCPP-M > HCPP-N = FMPP-M

> RPP-M > RPP-N > COPP-M

The values of tan δ of the wood–PP composites were as follows:

COPP-M > RPP-M ≥ RPP-N

≫ HCPP-N ≥ HCPP-M = FMPP-M

The activation energies of high-crystalline PP with MAPP or the nucleating agent were about 373 and 369 kJ/mol, respectively, and those of the regular PP with MAPP or the nucleating agent were 275 and 276 kJ/
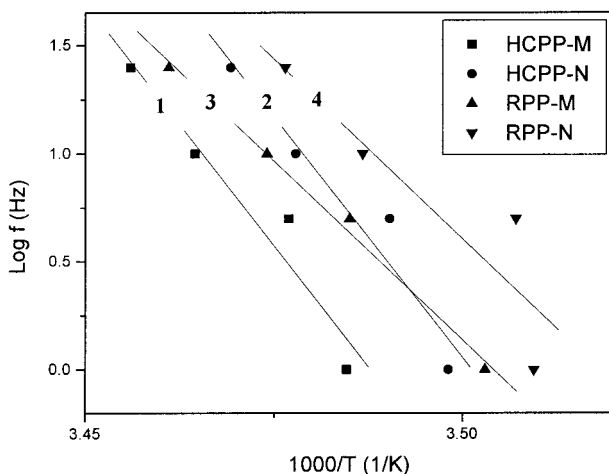
1 : $y = -44.849x + 156.42$, $R^2 = 0.9354$
2 : $y = -44.409x + 155.49$, $R^2 = 0.9357$
3 : $y = -33.085x + 115.94$, $R^2 = 0.9937$
4 : $y = -33.199x + 116.80$, $R^2 = 0.8136$

Figure 11 Regression-line equation to calculate the activation energy.

mol, respectively. Also, the activation energy of the impact copolymer PP treated with MAPP was about 140 kJ/mol, the lowest value of all the composites. Consequently, the wood–PP composite that exhibited a high activation energy is presumed to have an adhesion or interphase development between the polymer and the filler, resulting in better mechanical performance under similar conditions.

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