Characterization of Rheological and Thermophysical Properties of HDPE–Wood Composite

Mosfafa Tazi,[1] Fouad Erchiqui,[1] François Godard,[1] Hamid Kaddami,[2] Abdellah Ajji[3]

[1]Université du Québec en Abitibi-Témiscamingue, École de génie, Rouyn-Noranda Quebec, Canada
[2]Université Caddi Ayad Marrakech, Laboratoire 'LCO2MC,' B.P. 549, Marrakech 40000, Maroc
[3]Chemical Engineering Department, Polytechnique, Montreal, Quebec, Canada
Correspondence to: F. Erchiqui (E-mail: Fouad.Erchiqui@uqat.ca)

ABSTRACT: The objective of this study is to develop a new biocomposite material with high deformation ability. In this regard, the thermal, rheological, and thermophysical properties of this new composite were characterized as a function of temperature and filler concentration. High density polyethylene (HDPE) was the matrix of this new composite which was reinforced with six sawdust concentrations 0%, 20%, 30%, 40%, 50%, and 60%. Maleic anhydride grafted polyethylene (PE-g-MA) was used as coupling agent. Addition of sawdust with PE-g-MA increased significantly the complex viscosity, the storage modulus (G'), and loss modulus (G'') of the matrix. The superposition of the complex viscosity curves using temperature dependent shift factor, allowed the construction of a viscosity master curve covering a wide range of temperatures. Arrhenius law was used for the relationship of the shift factor to temperature. Furthermore, method of Van Gurp and Palmen (tan delta vs. G^*) is also used to control the time–temperature superposition. The experimental results can be well fitted with the cross rheological model which allowed the prediction of the thermorheological properties of the composites over a broad frequency range. By increasing wood concentration, both the activation energy and relaxation time for the biocomposites determined using, respectively, the Arrhenius law and the cole–cole rule increased. By contrast, specific heat of the matrix decreased with sawdust addition while its dimensional stability improved. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40495.

INTRODUCTION

Nowadays, due to the environmental and economic concerns, many research activities are directed toward the development of new composites based on thermoplastic matrices with plants (or their residues) reinforcement.[1] Reinforcement of composites with natural fillers has several advantages in comparison to mineral fillers including lower density, being inexpensive, and being non-abrasive. In fact, high cellulose component of natural fillers makes them easily biodegradable and recyclable. Also, cellulose fillers possess a crystalline structure which plays a positive role in the composite reinforcement. As a consequence many researchers are interested in the development of new techniques for extraction and modification of cellulose fillers from bioresources.[2]

In addition, cellulose has a reactive functionality that can react with coupling agents thus enhancing adhesion between the fiber and the matrix.[3] Studies have also shown that the mechanical properties of composites are highly dependent on the interaction between the thermoplastic matrix and distribution of loaded fillers.[4] While this interaction is well established, the loading force will be transferred from matrix to fillers more effectively.

On the other hand, the majority of modeling and simulating work of these biocomposites for their processing assumes constant thermal parameters of the materials, such as density and heat conductivity, or they do not take into account the special temperature dependency of the specific heat due to melting process. This is because the temperature dependence of these material parameters for biocomposites is not well understood sufficiently so far. Since the rheological and deformation behaviors are strongly connected with the thermal behavior, it became obvious that these issues affect directly the accuracy of any simulation or modeling result.

In this regard this study attempts to focus on the effect of temperature and bio-reinforcement contents on dynamic rheological, thermal, and physico-chemical properties of thermoplastic matrix composites (high density polyethylene [HDPE]) and bio-reinforcement fillers (sawdust).

Table I. Average Geometrical Dimensions of Fillers

Area (mm^2)	Long axis (mm)	Short axis (mm)	Shape ratio (L/D)
0.1154	0.52	0.30	1.97

MATERIALS

The sawdust used in this study was supplied by Tembec sawmill located in Béarn (QC, Canada). It consists of 65% white spruce (*Picea glauca*), 20% of black spruce (*Picea marica*), and 15% balsam fir (*Abies balsamea*). The particle size analysis of the sawdust is performed on more than 5000 particles using the apparatus Fiber Quality Analyzer (FQA, Optest Equipment, Hawkesbury, ON). Table I shows the average geometry of sawdust. Wood flour was sieved to a diameter <700 mμ ($\varnothing$ < 0.7 mm). The polymer matrix is a HDPE (SclairA59), with the melting temperature of 138°C, and density of 980 kg/m^3. The coupling agent is Fusabond 226 from Dupont, which is a polyethylene grafted with maleic anhydride (melting temperature 120°C, melt flow index [MFI] of 1.5 g/10 min, under condition 190°C, 2.16 kg). The used amount of coupling agent is 3% of total weight of composite. This amount is well known to improve the homogeneity of the mixture ensuring better distribution of fibers in the polymer matrix.[5,6] The sieved sawdust was previously dried under temperature of 105°C for 24 hours and stored in polyethylene bags. The residual moisture content in wood used for sample preparation is estimated by a second drying at 120°C for 24 hours. The wood humidity amount calculated from the mass of sawdust before and after drying was found <3 wt %.

METHODS

The composite samples were prepared using a twin-screw counter-mixer (Haake rheometrix with roller rotors) with angular speed of 90 rpm at a temperature of 170°C. In fact, this temperature is lower than wood fibers degradation temperature (200°C).[7] To prepare the composite material, first, Sclair A59 (HDPE polymer) and Fusabond (coupling agent) were mixed for 2 min in order to insure complete melting of the materials.

Then, sawdust was added to the mixture and blended for 5 min. Six different sawdust proportions were investigated including 0 wt %, 20 wt %, 30 wt %, 40 wt %, 50 wt %, and 60 wt%, and the total mass of composite in mixing chamber was 148 g. In the next step, flat disc samples were prepared by compression molding using a hot press at the temperature of 150°C (above melting temperature of the polymer, 138°C) with aluminum mold plates. In order to make sure the mixture is softened properly, a preload was first applied for 2 min. This preload is also beneficial for removing possible accumulated air in the material. Then, loading on the material was continued up to 8 MPa for 4 min to give the final circular shape of the samples with 20-mm diameter and 4-mm thickness (Figure 1).

CHARACTERIZATION OF BIOCOMPOSITES

Thermal Stability Tests

During the blending process and sample preparation, wood fillers are subjected to thermal degradation if the temperature exceeds 200°C, and thus all the tests are performed under this temperature. To monitor fiber thermal stability with increasing temperature, a thermogravimetric analysis study of the fiber reinforced composite was performed (TGA). The results are presented in Figure 2.

As can be seen clearly from Figure 2(b) the first two peaks correspond to degradations of hemicelluloses and cellulose of wood fiber. In fact, hemicelluloses degrades at low temperature between 220°C and 280°C while cellulose degrades between 280°C and 300°C.[8] The third peak in Figure 2(b) correspond to degradation of polymer which occurs at 500°C. The weight early lost observed between 100°C and 150°C [Figure 2(a)] corresponds mainly to water evaporation. This weight loss increases with the weight fraction of saw dust in the composite.

Rheological Characterization

The rheological measurements were conducted using the RS75 Haake rheometer with parallel plate configuration (PP20) equipped with a temperature controller TC500. The melted samples were subjected to a frequency sweep (0.1–100 Hz) using controlled deformation in the linear region. For this purpose,

Figure 1. Pellets (left) and compression molded samples (right) of wood–polymer composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
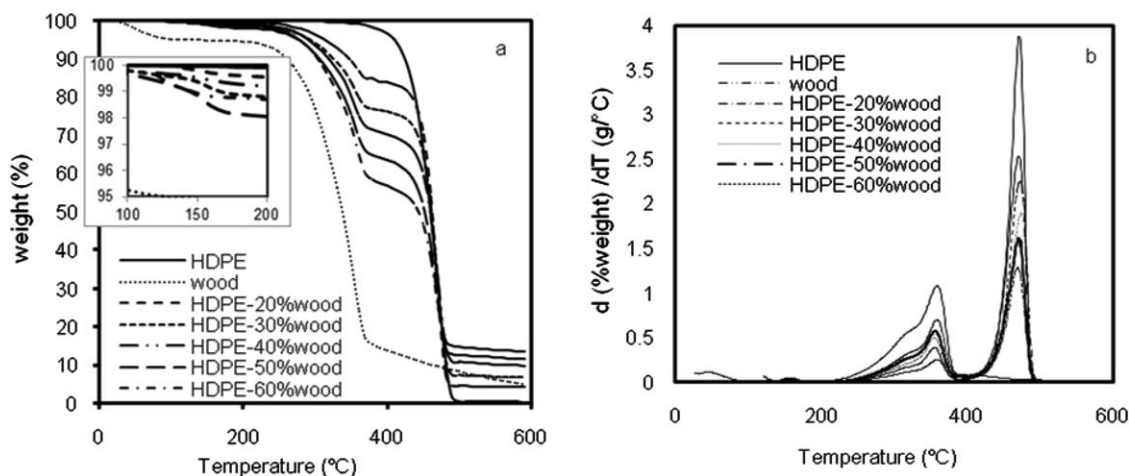
Figure 2. Thermal stability tests of wood plastic composites. (a) Weight change of materials by increasing temperature. (b) First derivative of change weight to temperature by increasing temperature.
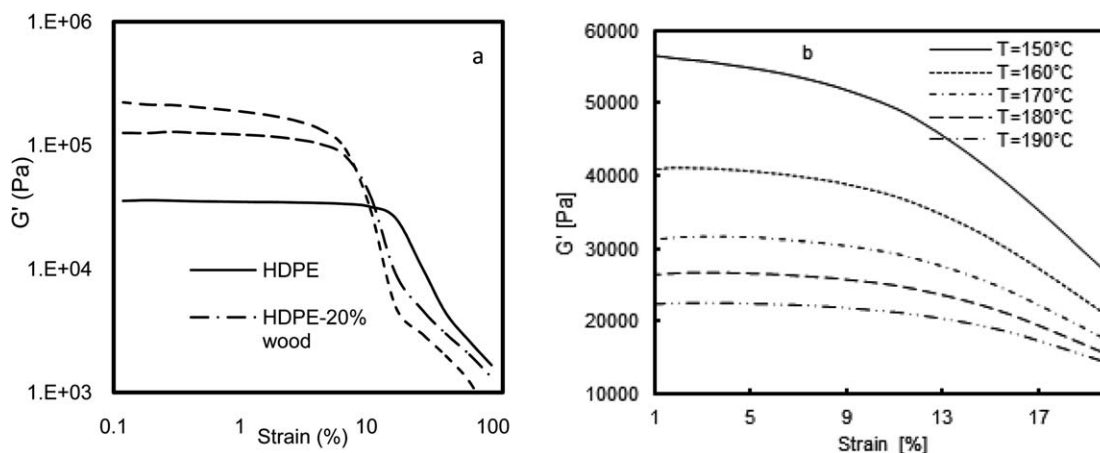
Figure 3. Alteration of linear regions of deformation (a): Effect of different fillers content on the linear deformation region of biocomposites at T = 170 °C, (b) Effect of different temperature on the linear deformation region of HDPE.

an amplitude sweep at constant frequency (equal to 10 Hz) was performed with samples at different fillers contents [Figure 3(a)] and at different temperatures [Figure 3(b)] to identify any changes in the linear region. Based on Figure 3, the linear region of deformation curve decreases while fillers content increases and increases while temperature increases.
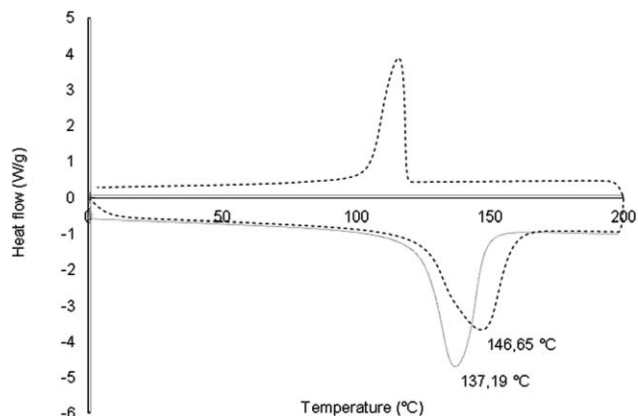
Morphological Characterization

For morphological characterization, samples were analyzed with scanning electron microscopy (SEM). In this case, samples were fractured in liquid nitrogen and coated with a thin film of gold in a sputter coater in order to eliminate electron charging. The coated samples were then observed at different resolutions using a voltage of 10 kV.

Thermal Properties Analyses

The thermophysical properties of the biocomposites were analyzed using DSC Q400, TA instrument series. The measurement procedure is shown in Figure 4. All samples are heated to a temperature of 200°C with a rate of 20°C/min and kept at this temperature for 10 min. The purpose of this test procedure is to eliminate any residual stresses in the samples which might be

accumulated during the thermal history of the samples. Then, from the liquid state, samples are cooled at a rate of 20°C/min to the solid state. After this first cycle, a second heating is performed. Samples were tested in an inert environment of nitrogen gas. We noted that the melting temperature of the polymer

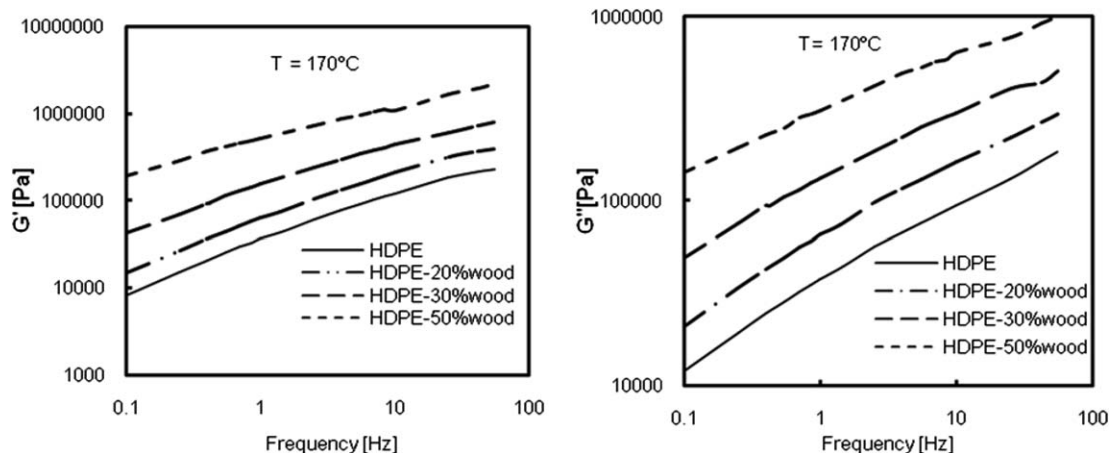**Figure 4.** The measurement procedure of calorimetric characterization for HDPE.

Figure 5. Effect of filler content on rheological modules (G' and G'') at 170°C.

shifted to lower values during the second heating cycle. The melting temperature of the HDPE was estimated equal to 137.2°C ± 1 C.

RESULTS AND DISCUSSION

Thermorheological Characterization

In the case of rheology, interaction between polymer and fillers is the most prominent factor; hence, better understanding of interfacial properties is necessary.

Basically, addition of wood fillers to polymers results in increase of the melt rheological behavior of composites.[9] Interfacial modification with coupling agent (PE-g-MA) also found to increase the melting behavior of the filled polymers during processing.[4,10–12] Numerous authors have investigated the effect of addition of coupling agent on the rheological behavior of wood plastics composites. On the other side, rheology has been widely used to assess the morphology and interfacial status of polymer blends, alloys, and filled polymers. Certain author has studied the rule of the rheological method to model interfacial effect on material properties and structure.[13]

Effect of Concentration on the Dynamic Properties

Dynamic Modules. Figure 5 shows the changes of the dynamic modulus (G') and (G'') as function of frequency and sawdust content. At low frequencies, the viscous properties are dominant compared with the elastic ones whereas at high frequencies we observe an opposite behavior. Composite materials at crossing points (crossover frequency) show the same elastic behavior as viscous. In addition, the dynamic storage modulus (G') and dynamic loss modulus (G'') increase with the filler content, while their crossover frequency is decreased and take place at lower frequency (Figure 5). This may clarify the point that at high filler loadings the behavior of the composites is more elastic. Table II shows the values of the crossover frequencies of the composites at different fillers concentrations. On the other hand the reduction of the frequency of the crossing point indicates an increase of the relaxation time of the polymer that could be explained by good interaction with the filler particles.

Complex Viscosity. The complex viscosity curves are shown in Figure 7. It can be clearly seen that the introduction of sawdust

Table II. Crossover Frequency for Different Wood Concentrations

Fillers load (%)	$G' = G''$ (Pa)	Frequency (Hz)
0	44,200	1.485
20	73,890	1.394
30	93,840	0.425
40	71,100	0.1833
50	55,750	0.003798

induces a significant increase of the complex viscosity. This effect is even more pronounced when the content of the filler is increased. As can be seen from Figure 7(b), at 60% filler content, dynamic viscosity of composite is more than 100 times higher than the neat polymer which make the processing and blending of composite more difficult. Moreover, increase of fillers content brought no yields behavior in rheological behavior of wood HDPE composite. Yield stress describes how strong is the interaction of particle to adjacent particle in which directly is in relation with particle size. There are many literatures regarding yield stress behavior of thermoplastics polymers with
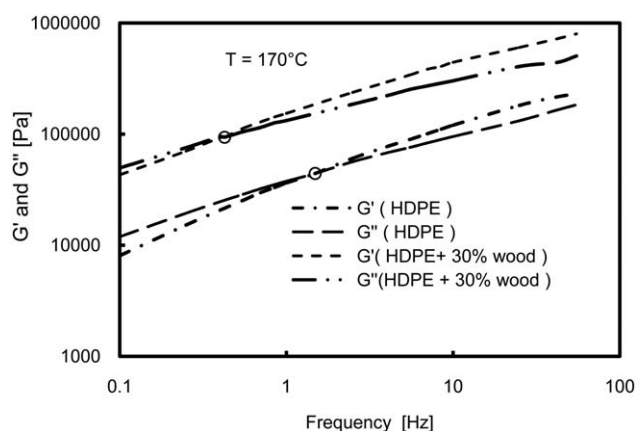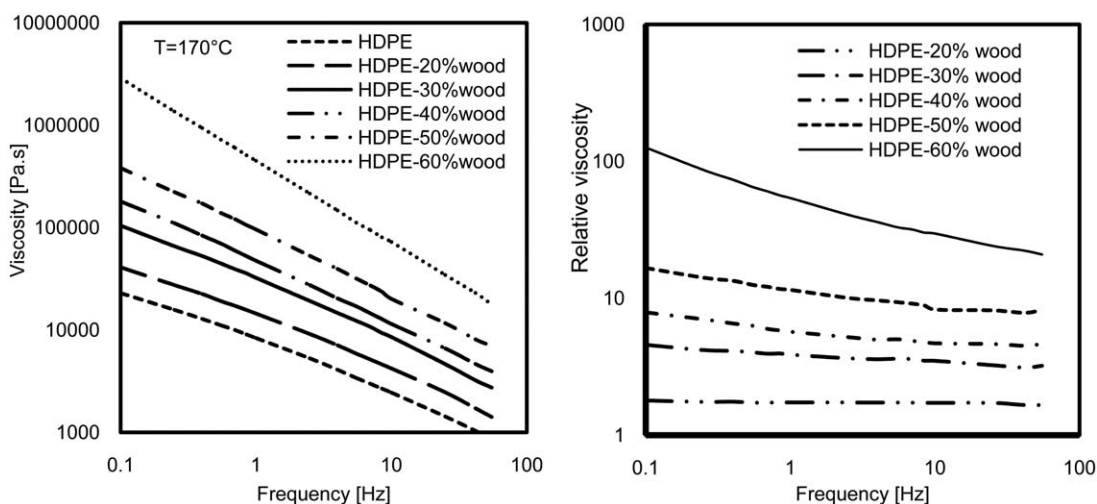

**Figure 6.** Crossover points of the composites modulus.

Figure 7. Complex viscosity of the composites at different fillers concentrations (left, a) and the ratio between the viscosity of the composite and the viscosity of the polymer matrix (right, b).

inorganic fillers.[14] Certain authors report that yields behavior for wood polymer composite is in relation with particle size and is generally manifested in case of particles below 0.5 μ.[15]

Effect of Temperature on Rheological Properties

Temperature affects significantly the dynamic mechanical properties of wood plastic composites. Changes in dynamic modulus
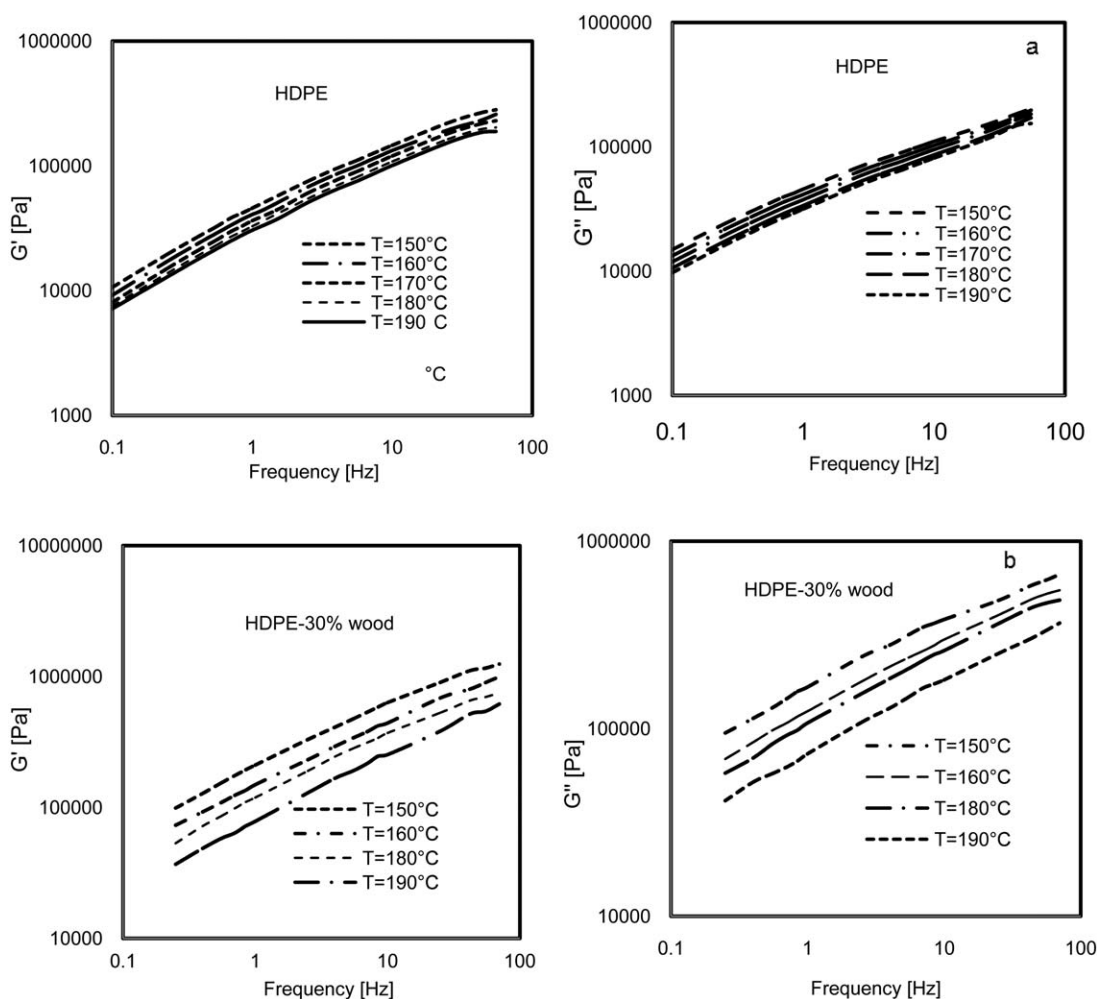
Figure 8. Storage (G') and loss modulus (G'') at different temperature of neat HDPE (a) and the composite with 30% sawdust (b).
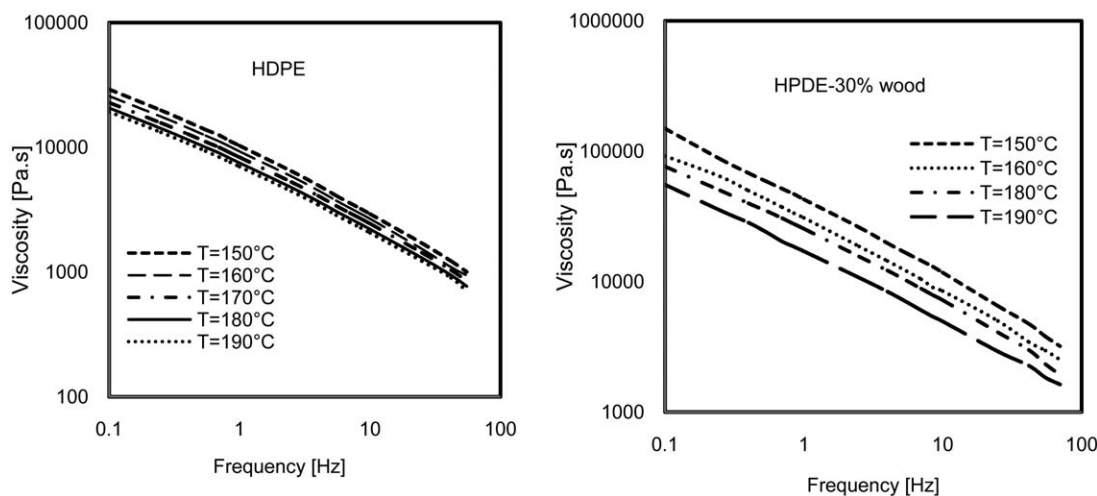
Figure 9. Variation of complex viscosity of the polymer (HDPE) and the composite (HDPE-30% fillers) at different temperatures.

(G', G'') of the two materials (HDPE, HDPE + 30% sawdust) with temperature are shown in Figure 8(a,b); the temperature varies between 150°C and 190°C. As can be seen from these figures, by increasing the temperature dynamic modulus of the neat HDPE and the composite decrease.

Complex Viscosity. The complex viscosity of the HDPE and the HDPE-composite decreases when frequency is changed from 0.1 to 100 Hz. On the other hand the complex viscosity decreases significantly when temperature increases (Figure 9). Remarkably, presence of wood fillers make the viscosity more sensitive to temperature, which could be attributed to internal humidity of wood fillers.

Dynamic Thermomechanical Analysis

In order to have a successful modeling and simulation of forming process of wood plastic composite, (thermoforming, injection stretch blow molding, etc.), it is essential to know the viscoelastic behavior of the used materials. For example, in injection process, it is important to know the alteration of the viscosity versus the temperature. In the following paragraphs, the results of the dynamic thermomechanical analysis of biocomposites with different loads are presented regarding the effects of temperature on the viscoelastic behavior. Dynamic viscosity curves were superposed, using a temperature dependent shift factor (a_T). This superposition allows us to obtain viscosity masters curves. Figure 10(a) shows the changes of reduced complex viscosity (η/a_T) as a function of reduced pulsation ($\omega \cdot a_T$)

The superposition was carried out at a reference temperature of 170°C for all materials. The master curves adjustment is made using rheological model, cross model [eq. (1) below]. This allowed us to define a unique behavior for each composite at different frequencies and temperatures; this behavior is described by eq. (1) in which the dynamic viscosity (η) is plotted as a function of shear rate in the following form.

$$\eta = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{(1 + (\frac{\omega}{\omega_b}))^n} \qquad (1)$$

where η_0 is the Newtonian viscosity of plateau; η_∞ is the infinite viscosity; n is the dependence degree of dynamic viscosity
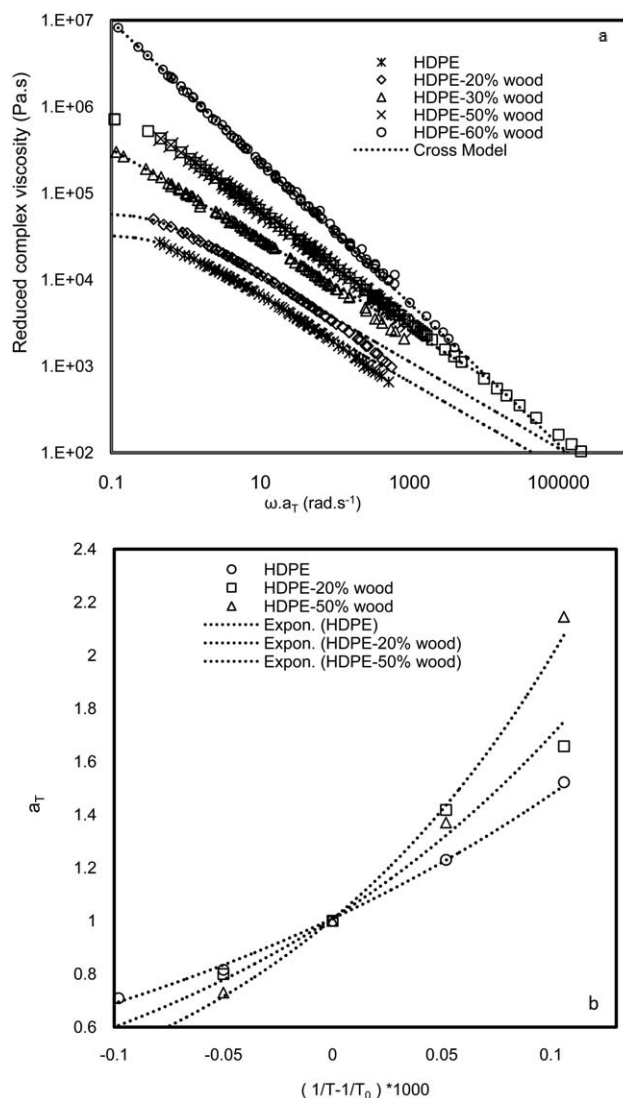
Figure 10. Master curves and variation of activation energy of the composite. (a) Reduced complex viscosity versus reduced pulsation. (b) Shift factors (a_T) versus temperature.

Table III. Rheological Parameters of the Composites

Materials	η_∞ (Pa s)	η_0 (Pa s)	n	ω_b (rad/s)
HDPE	0	0.491e + 04	0.4629	16.41
HDPE-20% wood	0	1.471e + 04	0.4417	7.163
HDPE-30% wood	0	3.119e + 05	0.2610	0.0001453
HDPE-40% wood	0	7.641e + 05	0.2829	0.0001809
HDPE-50% wood	918.6	2.093e + 07	0.4532	6.833e − 06
HDPE-60% wood	1.237e + 04	1.260e + 08	0.5980	1.378e − 06

toward shear rate (which is a function of the slope in power region of the curve); and ω_b is the cross constant (frequency at which viscosity drops rapidly). The comparison of the master curves data with rheological model (Cross model), allowed us to predict the rheological behavior of the biocomposites at different temperatures out of the experimental temperature range we used. Table III presents the parameters characteristic of the studied materials [Newtonian viscosity (η_0), viscosity at infinite (η_∞), relaxation time ω_b and index n] obtained through model fitting.

**Mathematical Description of the Temperature Dependence**

The shift factor $a_T(T)$ contains all the information concerning the temperature dependence of the material. In order to quantify this information and to get tool for further application, the shift factor has to be described by a mathematical equation. There are two well-known relationships for the description of the temperature dependence of polymers: Arrhenius law and Williams Landrel and Ferry (WLF) equation. The preferable model depends on the material, the temperature range of interest as well as the glass transition temperature T_g. Just above the glass transition temperature, the thermal simulated flexibility of one polymer chain depends on its adjacents (cooperative process), but while temperature is above T_g, the thermal flexibility

of polymer chains are more dependent on the dynamic flow properties. This difference in the physical behavior of polymers requires different mathematical descriptions. WLF equation describes $a_T(T)$ above the glass transition temperature of (linear) polymers and is approximately valid in the temperature range $T_g < T < T_g + 100$ K. On other hand, Arrhenius equation describes shift factors of the most polymers at temperatures above the glass transition ($T > Tg + 100$ K). The analysis of $a_T(T)$ by using Arrhenius law determines activation energy of the composites. Figure 10(b) shows the shift factor (a_T) as a function of temperature.

$$a_T = k \cdot \exp - \frac{E_a}{R(T - T_0)} \qquad (2)$$

where E_a is the activation energy (kJ/mol); R is the universal constant of perfect gases (it is 8314 J/mol K); k is the constant; T_0 is the reference temperature; and T is the temperature.

Activation energy represents the potential energy barrier that allows the relaxation process of macromolecular chains of the polymer. The activation energy of HDPE polymer is estimated to be 29.8 ± 1 kJ/mol which is comparable to the value found in literature. In fact, Schott and Kaghan evaluated the activation energy of HDPE to 29.26 kJ/mol.[16] The addition of wood fiber and coupling agent increased the activation energy which in our case and was estimated to 32.52 kJ/mol and 39.30 kJ/mol for 20
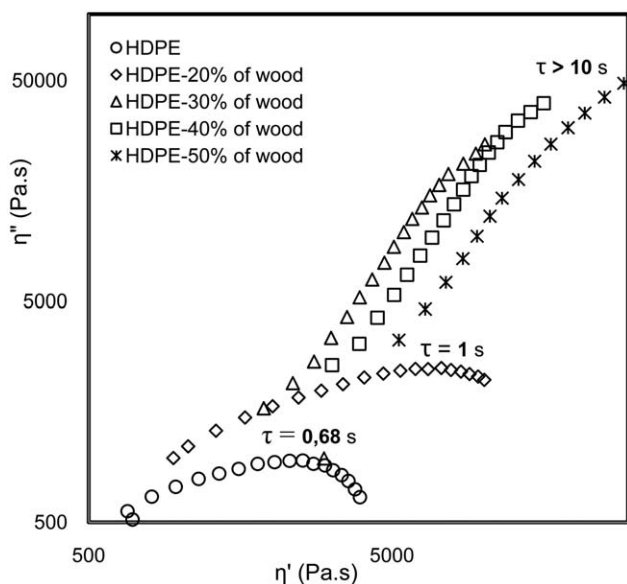
Figure 11. Cole–cole plot used to determine the relaxation time of wood HDPE composite.
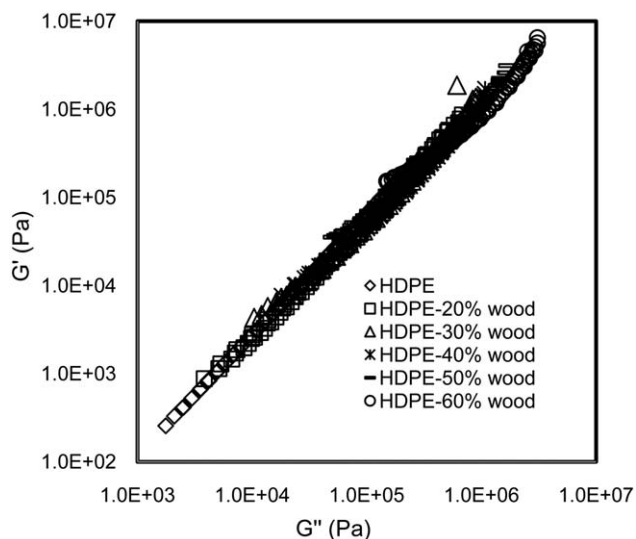
Figure 12. Log G' versus log G'' to verify the simplicity of thermorheological wood HDPE systems.
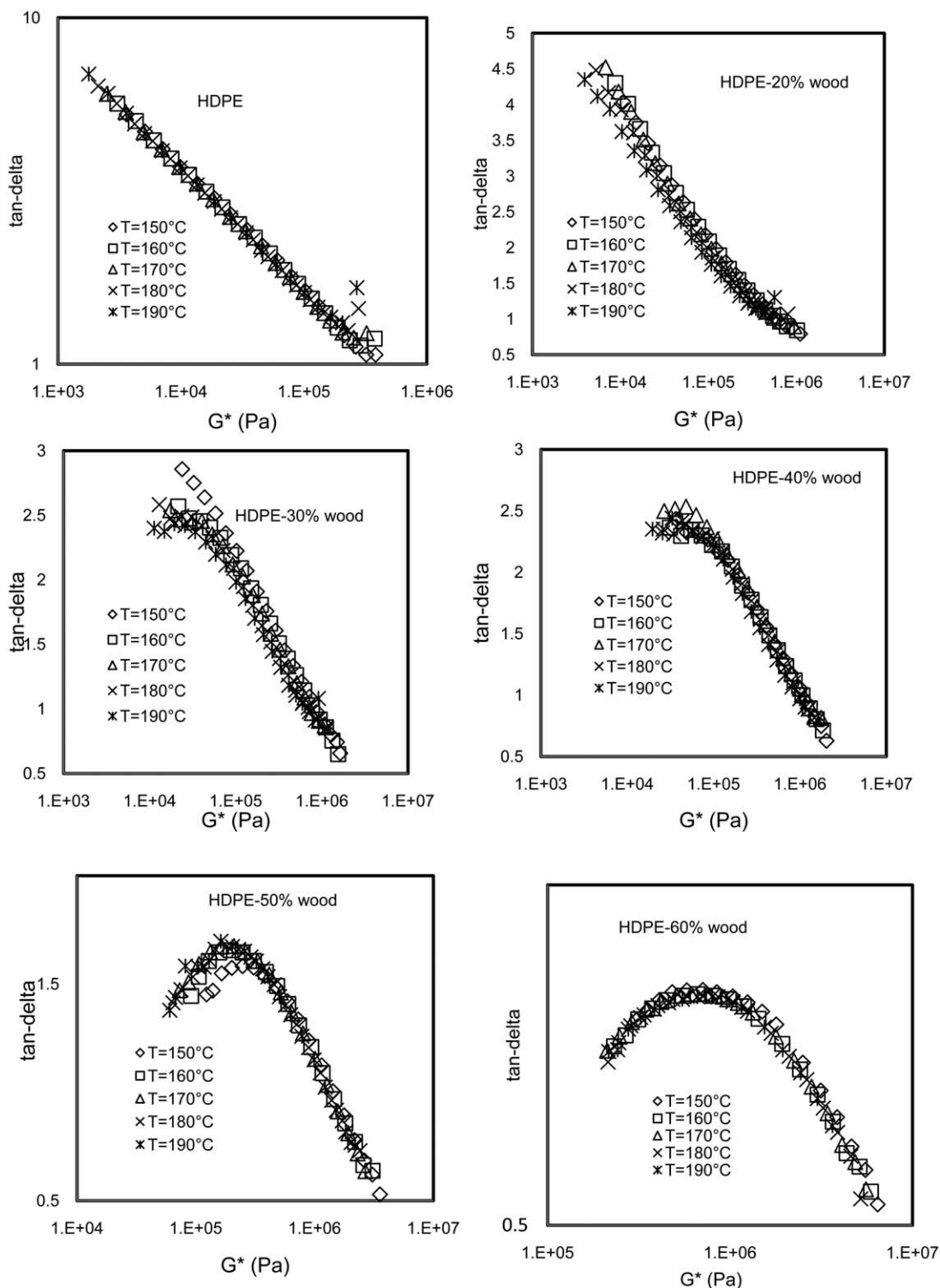
Figure 13. Van Gurp and Palmen curve (tan-delta vs. G^*) for wood–HDPE composite.

wt % and 50 wt % of filler based composites, respectively. This increase is more due to the incorporation of sawdust, than the chemical modification of polymer by coupling agent reaction (PE-g-MA). This later induces higher interactions between the polymer and the filler which lead to an increase of the polymer relaxation time. This results is in good concordance with the decrease of the frequency at the crossing of G' and G'' which is observed and presented in. Furthermore, in this article, Cole–Cole plotting technique is used to study the relaxation difference between the polymer and composites.[17] This is a useful technique to obtain some important viscoelastic properties of polymers and composites. The imaginary versus real parts of
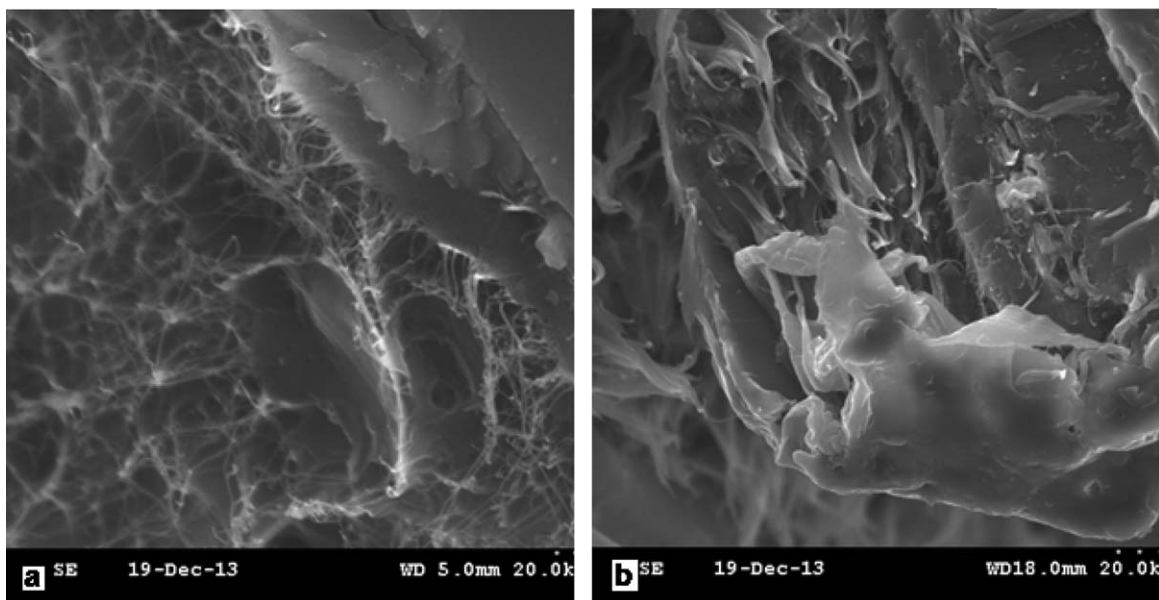
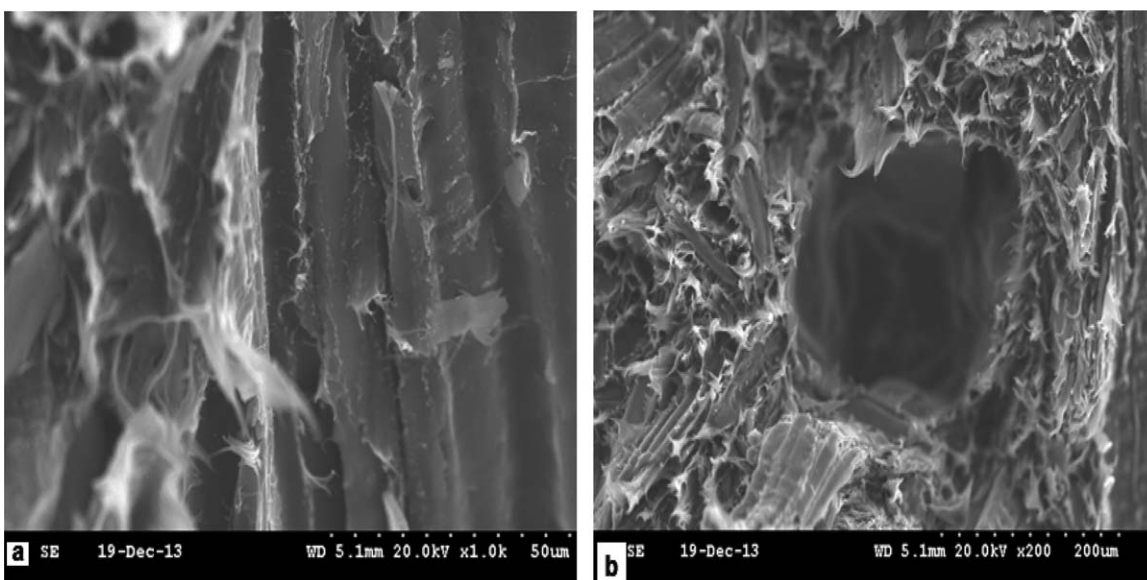**Figure 14.** SEM micrographs of the fractured surface of HDPE-40% wood composite with coupling agent.

Figure 15. SEM micrographs of fractured surface of HDPE-40% wood composite without coupling agent.

Table IV. Thermophysical Parameters of the Composites

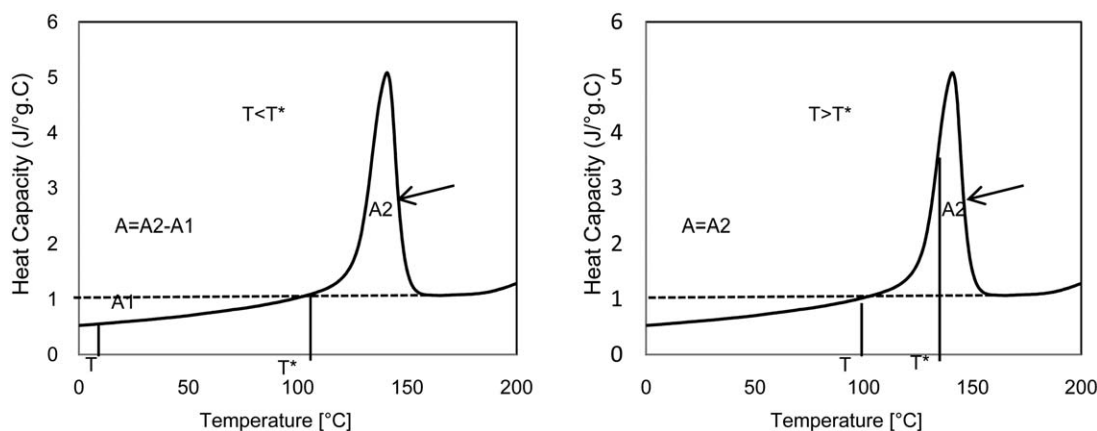| Composites	T_m (°C)	ΔC_p (J/g/°C)	ΔH_m (J/g)	X (%)
HDPE	138.19	16.78	215	74.65
HDPE-20% wood	142	14	169.8	76.57
HDPE-30% wood	143.32	11	150.8	78.15
HDPE-40% wood	140.03	10	128.8	78.46
HDPE-50% wood	143.36	6	107	79.05
HDPE-60% wood	140.9	4	90.74	85.15

Figure 16. DSC curves used to calculate changes in the biocomposites enthalpy.

the complex viscosity function are shown in Figure 11 and are also used to determine the relaxation time of neat polymer and composites. From the frequency corresponding to the maximum value of η'' at the circular arc, we can determine the weight-average relaxation time, it is evident that addition of wood fillers increase the relaxation behavior of composite. Relaxation time of neat polymer, composite with 20% wood filler, and the rest of composite assessed, respectively 0.68, 1, and higher than 10 seconds.

Based on obtained results, increase in filler content makes the behavior of composite more elastic due to the better interaction between filler and matrix.

However, even if the time–temperature superposition (tTS) principle is used principally for homogeneous (amorphous) polymers. This principle could also be used for composite materials when thermorheological behavior simplicity is checked. The above presented results are meaningless if the thermorheological behavior simplicity is not checked. In order to verify the thermorheological simplicity of the studied systems, a plot of log G' versus log G'' for all the wood polymers composites were performed.[18] As can be seen from Figure 12,

the data points fall on a common line in a log G' versus log G'' presentation, also the dispersion in the data is too narrow. Such notes validate the tTS principle of polymer and wood–polymer composites; furthermore, method of Van Gurp and Palmen (tan delta vs. G^*) is also used to control the tTS (Figure 13). Similar, results obtained even though some deviation happened at low frequency in which can be interpreted by low interaction between wood fillers and polymer at low frequency.

Morphological Structure Analysis

To investigate the interface of wood flour particles and polymeric matrix, we used SEM (Figures 14 and 15). As can be observed from Figure 14, addition of coupling agent leads to significant improvement of interfacial adhesion. In fact, coupling agent provides excellent coupling effect between wood fillers and HDPE matrix. As can be seen from Figure 14, disappearance of the interfacial gap between filler and matrix confirms a ductile deformation of matrix. In opposite, samples without coupling agent Figure 14 contains a void resulting from pull out of fillers; in addition, there is an interfacial gap
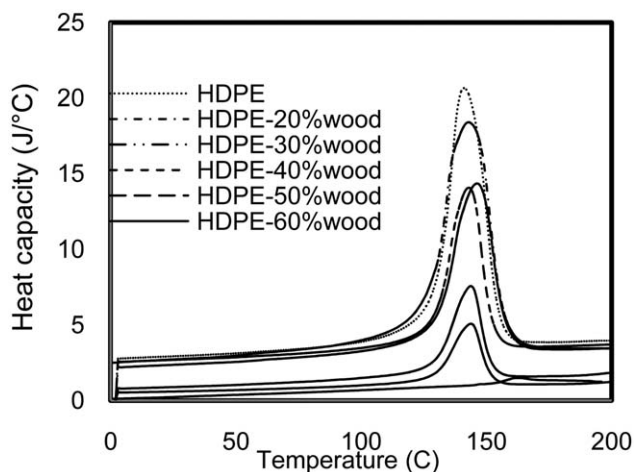

Figure 17. Change of heat capacity of HDPE–wood composite as function of temperature.
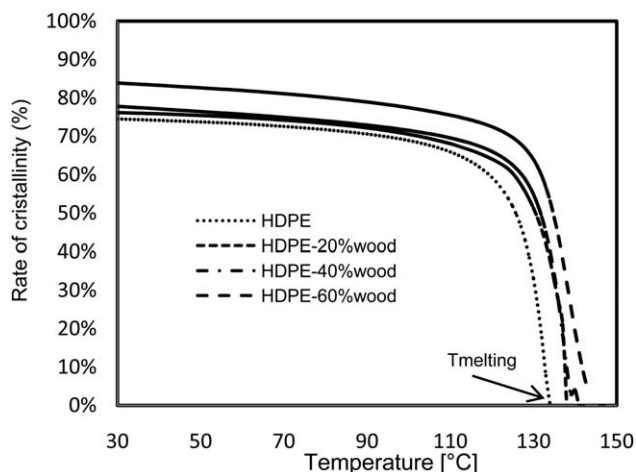

Figure 18. Change of HDPE crystallinity rate of HDPE–wood composite as function of temperature.

between fiber and matrix (Figure 14) which indicates inappropriate adhesion between filler and matrix.

Differential Scanning Calorimetry (DSC) Analysis on Biocomposites

The DSC results on the studied materials are presented in Table IV. The addition of wood fillers and coupling agent (PE-g-MA) to the polymer matrix resulted in an increase of the melting temperature (T_m) of HDPE up to value higher than 141°C as shown in Table IV. The same phenomenon was reported in literature.[19,20] The shift of melting temperature of HDPE could be attributed to the increased level of crystallization which favored by nucleation effect of fillers. Generally fillers act as nucleation sites for macromolecular chains by lowering the germination potential of polymer.[20]

Measurement of Heat Capacity and Crystallinity Rate as Functions of Temperature

The specific heat of biocomposites is an extremely important thermal property. It provides information on the flexibility of macromolecular chains and parts. Specifications obtained—for example, enthalpy (H), entropy (S), and internal energy (U)—can, in turn, inform us on the physical state of biocomposites. Table IV shows the thermophysical parameters of the biocomposites as function of fillers content. Data curves of DSC analyses were used to evaluate the heat capacity of biocomposites. We noticed that during the melting phase, the variation of heat capacity (ΔC_p) of wood–HDPE composites decreased compared with the neat matrix; 16.78 J/g °C for polyethylene versus 4 J/g °C for HDPE–60% wood fillers, as shown in Table IV. This could be interpreted in the way that the wood fillers act as a hindrance of molecular chains mobility close to melting temperature. C_p curves are also used to analyze the changes of the crystallinity degree (X%) of the polymer in biocomposites depending on temperature. The degree of crystallinity is calculated using the following equation:

$$X(\%)(\text{T}) = \frac{[A]_T \times (100/w(\%))}{\Delta h(T)_M} \quad (3)$$

where $[A = A2 - A1]_T$ is the changes in enthalpy based on temperature (see Figure 16); w is the weight percentage of HDPE; $\Delta h(T)$ is the changes in enthalpy of HDPE while being 100% crystalline.

Figure 17 shows change of heat capacity of composite as functions of temperature and filler content. Heat capacity decreases while the filler content increases. Figure 17 shows an extensive variation of heat capacity around melting temperature. The crystallinity degree of biocomposites remains constant at low temperature and then drops around the melting temperature. The addition of fillers to polymer matrix increases significantly the rate of crystallinity. It reached a level of 85% when the fillers content was 60%. Change of crystallinity degree with fillers content at different temperature is represented in Figure 18.

CONCLUSION

In this study the dynamic rheological properties of HDPE composites and sawdust at different fillers content and temperatures in the presence of a coupling agent was investigated. The results indicate that: (i) the storage modulus, loss modulus, and complex viscosity increase while fillers content increases and decreases while temperature increases; (ii) the superposition of the complex viscosity curves using temperature-dependent shift factor, allowed the construction of a viscosity master curve covering a wide range of temperatures; (iii) addition of wood fillers in polymer results in an increase of both relaxation behavior and activation energy of polymer chains, which can be explained by good interaction between wood particles and polymers chains. The experimental results can be well fitted with the cross rheological model which allowed the prediction of the thermorheological properties of the composites over a broad frequency range. By contrast, specific heat of the matrix decreased with sawdust addition while its dimensional stability improved.

REFERENCES

1. Erchiqui, F.; Godard, F.; Gakwaya, A.; Koubaa, A.; Vincent, M.; Kaddami, H. *Polym. Eng. Sci.* **2009**, *49*, 1594.

2. Kaddami, H.; Dufresne, A.; Bendahou, A.; Sautereau, H.; Sami, N. *Compos. Part A: Appl. Sci. Manuf.* **2006**, *37*, 1413.

3. Faruk, O.; Bledzki, A. K.; Fink, H. P.; Sain, M. *Prog. Polym. Sci.* **2012**, *37*, 1552.

4. Bledzki, A. K.; Reihmane, S.; Gassan, J. *Polym. Plast. Technol. Eng.* **1998**, *37*, 451.

5. Keener, T.; Stuart, R.; Brown, T. *Compos. Part A: Appl. Sci. Manuf.* **2004**, *35*, 357.

6. Sombatsompop, N.; Yotinwattanakumtorn, C.; Thongpin C. *J. Appl. Polym. Sci.* **2005**, *97*, 475.

7. Burgstaller, C. *Monatsh. Chem.* **2007**, *138*, 343.

8. Ramiah, M. *J. Appl. Polym. Sci.* **2003**, *14*, 1323.

9. Li, T.; Wolcott, M. P. *Compos. Part A: Appl. Sci. Manuf.* **2004**, *35*, 303.

10. Hristov, V.; Vlachopoulos, J. *Macromol. Mater. Eng.* **2007**, *292*, 608.

11. Li, T.; Wolcott, M. *Polym. Eng. Sci.* **2005**, *45*, 549.

12. Saheb, D. N.; Jog, J. *Adv. Polym. Technol.* **1999**, *18*, 351.

13. Lamnawar, K.; Maazouz, A. *Rheol. Acta* **2008**, *47*, 383.

14. Gloaguen, J.; Lefebvre, J. *Polymer* **2001**, *42*, 5841.

15. Minagawa, N.; White, J. L. *J. Appl. Polym. Sci.* **1976**, *20*, 501.

16. Schott, H.; Kaghan, W. *J. Appl. Polym. Sci.* **1961**, *5*, 175.

17. Zhang, H.; Lamnawar, K.; Maazouz, A. *Rheol. Acta* **2012**, *51*, 691.

18. Zhang, H.; Lamnawar, K.; Maazouz, A. *Macromolecules* **2012**, *46*, 276.

19. Bendahou, A.; Kaddami, H.; Sautereau, H.; Raihane, M.; Erchiqui, F.; Dufresne A. *Macromol. Mater. Eng.* **2008**, *293*, 140.

20. Bouafif, H.; Koubaa, A.; Perré, P.; Cloutier A. *Compos. Part A: Appl. Sci. Manuf.* **2009**, *40*, 1975.