EFFECTS OF CHEMICAL FOAMING AGENTS ON THE PHYSICO-MECHANICAL PROPERTIES AND RHEOLOGICAL BEHAVIOR OF BAMBOO POWDER-POLYPROPYLENE FOAMED COMPOSITES

Xiaxing Zhou, Lihui Chen,* and Qiaojia Lin

To make full use of bamboo resources in China and explore the foaming mechanism of bamboo powder-polypropylene (PP) foamed composites, a foamed composite of 54 wt% PP and 13 wt% HMSPP containing 33 wt% bamboo powder blends was prepared by injection moulding. Effects of chemical foaming agents (CFA) on the mechanical properties and rheological behavior of foamed composites were investigated. The mechanical measurements and ESEM test results indicated that the composite with 1% modified exothermic FA had smaller cell size and better cell distribution compared with endothermic FA. It also had better physico-mechanical properties, with a decrease of 14.2% in density and an increase of 16.8% to 40.2% in the specific tensile, bending, and notched impact strength compared with the non-foamed composite. The frequency sweep results indicated that all composites had a shear-thinning behavior, and both the modulus and complex viscosity of composite with 1% exothermic FA decreased compared with those of the non-foamed composite. The shear rate scans revealed that the non-Newtonian fluid index increased with the increase of exothermic FA content. The viscous activation energy of the modified composite with 1% exothermic FA was 46.41KJ·mol^{-1}. This was an increase of 8.9% compared with that of the non-foamed analogue.

Contact information: *College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, P. R. China. *Corresponding author*: lihuichen@263.net*

INTRODUCTION

Natural and wood fiber-plastic composites (WPCs) have environmental and economical advantages and have been extensively applied (Clemons 2002). However, WPCs have some shortcomings, such as a higher density and lower impact strength, which limit their industrial applications. Over the past decade, several researchers have studied the production of foamed WPC by using a chemical foaming agent (CFA) or a physical foaming agent (PFA) such as water, argon, carbon dioxide, or nitrogen (Lee 2008; Faruk *et al.* 2007). It has been reported that a cellular WPC with a fine micro-cellular structure can achieve outstanding cost-to-performance ratio and has a favorable strength-to-weight ratio compared to its non-foamed analogue. Due to these unique properties, foamed WPC has been widely used in many fields, especially in the construc-

tion and automotive industries, in place of wood, plastic, glass fiber, metal, and other composites.

The first matrix resin used for foamed WPC was polystyrene (PS) (Rizvi *et al.* 2000), and current research has focused on the study of polyvinyl chloride (PVC)-based and polyolefin-based foamed WPCs (Matuana *et al.* 1997, 1998; Nawadon *et al.* 2011). However, PS-based foamed WPC has already been prohibited because of its "white pollution" to the environment. In addition, PVC-based foamed composites always release dioxin, chlorine hydride, and other toxic gases during processing, use, and disposal. In contrast, PP is environmentally friendly, easily recycled and degraded, and also has better resistance to heat and chemical corrosion. Therefore, much attention has been paid to the PP-based foamed WPC. The research interest is primarily focused on the preparation technology, the fiber pretreatment, the cell morphology of the foamed composite, and the effects of the type and concentration of foaming agents on the mechanical and physical properties of foamed composites made with high-density polyethylene(HDPE)/PP/wood fiber (Rachtanapun 2003), microcellular PP/wood fiber composites (Zhang and Rodrigue 2005; Bledzki and Omar 2006a,b), and PP/flax fiber composite foams (Bledzki *et al.* 2005) .

The major plant materials that have been used as reinforcements for production of PP-based foamed composite are wood fiber, wood flour, and hemp fiber. China has been called the "bamboo kingdom" in recognition of its abundant bamboo resources, the longest history of the cultivation of bamboo, the largest acreage of bamboo forest, and the highest yield of bamboo production in the world. Bamboo possesses numerous advantages, such as low cost, acceptable specific strength, and high wear resistance (Lakkad and Patel 1980). Moreover, bamboo has demonstrated an ability to be a renewable and sustainable substitute for synthetic fibers. Unfortunately, presently the yield from the physical processing of bamboo is below 40% by weight. More than 60% of the bamboo timber becomes the processing residues in China (Zheng *et al.* 2005). The present work is based on an assumption that these processing residues may be suitable as the reinforcement in PP-based foamed composites.

It is difficult for PP to form a fine cell structure because of its narrow foaming temperature range. Moreover, the difficulty of foaming increases with the increase of bamboo powder content. The physical properties of the foamed composite will also be degraded if the cells are too large or are unevenly distributed. Therefore, it is important to explore foaming mechanisms and preparation technology of bamboo powder/PP foamed composites. In addition, the rheological behavior of composites affects not only the processing performance, but also the mechanical properties of the final product. However, it can be seen from the current information that the effects of foaming agents on the rheological behavior and viscoelastic properties of foamed WPC have been little reported. In this study, 54 wt% PP and 13 wt% HMSPP were blended and mixed with 33 wt% bamboo powder to prepare the foamed composite by injection moulding. The effects of the different types and contents of CFAs on the physico-mechanical properties, cell morphology, and rheological behavior of the foamed composite were investigated to obtain the bamboo powder/PP foamed composite with the highest strength-to-weight ratio and optimal rheological behavior.

EXPERIMENTAL

Materials

Moso bamboo (*Phyllostachys edulis*) powder with a mixture of particle sizes in the range of 90 to 450 μm and the density of 1.37 g/cm^3 was supplied by Lin-an Mingzhu Bamboo & Wood Industry Co., Ltd, in Zhejiang, China. PP (type of K8303) with a density of 0.90 g/cm^3, MI of 2.4g/10min at 230 °C, and a melting temperature of 168 °C from ExxonMobil Chemicals was used. High melt strength polypropylene, HMSPP (type of SMS-514F) with a density of 0.91 g/cm^3, a melting index (MI) of 3.2g/10min at 230 °C, and a melting temperature of 175 °C was provided by Korea Honam Petrochemical Ind. Co. With the intention of improving the compatibility between the bamboo powder, PP, and HMSPP, a maleic anhydride grafted polypropylene (MAPP) coupling agent from Nanjing Deba Chemical Co. Ltd, China was used. The coupling agent accounted for 9% of the weight percentage of the bamboo powder. Three types of CFAs were studied in this research. The exothermic FA azodicarbonamide (AC), with gas evolution of 240 mL/g and the endothermic FA with generated gas of 120 mL/g were obtained from Shanghai Jieyu Industry and Trading Co. Ltd, China. The gas evolution of exo-endothermic FA is 180 mL/g and it was purchased from Guangzhou Huike Chemical Co. Ltd, China.

Processing

Firstly, PP and HMSPP with MAPP, lubricant, and dried bamboo powder were mixed in a high-speed mixer (Henschel Mixer, type HM40 KM120) for 10 min. Bamboo powder was previously dried in oven at 100 °C for 10 h before mixing. The PP accounted for 54 wt%, the HMSPP accounted for 13 wt%, and the bamboo powder accounted for 33 wt% of the foamed composites. That is to say, the weight ratio of bamboo powder to plastic was 1:2; this ratio was selected because the previous studies reported that the comprehensive mechanical properties of foamed composite were best when the amount of bamboo powder was 33 wt% (Zhou *et al.* 2011). Secondly, the mixture was transferred to mix in a HAKKE mixer for 12 min at 180 °C with a rotational speed of 40 rpm. After that the blends were crushed into granules for injection moulding in a WSGM-250 mill. Lastly, the foaming agent and the bamboo powder-PP granules were mixed, and the foamed samples were prepared by injection machine at the melting temperature of 160-190 °C, the mold temperature of 90 °C, under an injection pressure of 5 to 6 MPa, a packing pressure of 4 MPa, a back pressure of 6 MPa, and a packing time of 10 s.

Measurements

Thermal analysis of CFAs

The thermal decomposition behaviors of CFAs were characterized using a TG-DTA (Netzsch STA449C) device at a heating rate of 10 °C/min in a nitrogen atmosphere from room temperature to 400 °C.

Physico-mechanical properties

The densities of foamed specimens were measured according to ASTM D792. The flexural properties in three-point bending mode and the tensile strengths were

respectively measured in accordance with ASTM D790 and ASTM D638 at a crosshead speed of 10 mm/min. The notched impact strength and the vicat softening point (VST) tests were respectively referred from ISO 8256-2005 and ASTM D1525-2000. Multiple measurements (8 runs) were conducted for all measurements, and a mean value was reported.

ESEM analysis

The tensile fractured surfaces of non-foamed and foamed composites were investigated by environmental scanning electron microscope (ESEM-XL30 PHILIPS) after being treated with gold sputtering.

Rheological behavior

The rheological measurements for the samples with the diameter of 30 mm and the thickness of 2.2 mm were investigated with a rotary rheometer (Haake ARSⅢ, Germany). The dynamic strain sweep test was conducted at 180 °C from 10^{-4} to 5% for determination of the linear viscoelastic region (LVR). A dynamic frequency sweep test was then conducted to measure the storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) within a frequency range from 0.01 to 100 Hz at 180 °C in the LVR. The dynamic shear rate sweep test was conducted at the shear rate amplitude from 10^{-3} to 30s^{-1} at 180 °C, and the shear rate scanning was carried out at different temperatures (160 °C, 170 °C, 180 °C, and 190 °C) to study their effect on the viscous activation energy of the composites. The temperature sweep tests were set up in a temperature range from 160 °C to 190 °C.

RESULTS AND DISCUSSION

Thermal Properties of CFAs

TG and DSC curves of three types of CFAs are shown in Fig. 1. As can be seen, the endothermic FA began to decompose at 110 °C and presented two endothermic peaks at 92.5 °C and 135.9 °C, respectively. The first region between 87.4 °C and 101.7 °C corresponded to the release of the adsorbed water. The other region between 119.2 °C and 169.6 °C was associated with the decomposition of the endothermic FA. The decomposition temperature of endothermic FA was far less than the melting temperature of the plastic; moreover, the generated gas disappeared easily at this moment. As a result, the endothermic FA was not suitable for use as a foaming agent in this WPC system. As for the exo-endothermic FA, the initial thermal decomposition temperature (T$_i$ 171.7 °C) was close to the melting temperature of the plastic, so it could be used directly. The DSC thermogram indicated that multi-level complex reactions occurred, including endothermic reactions at 106.6 °C, 171.6 °C, and 253.1 °C and exothermic reactions at 211.9 °C and 267.4 °C. With regard to the exothermic FA, the T$_i$ (205.8 °C) was much higher than the melting temperature of PP. At the higher temperature, the melt strength of PP decreased and the generated cell merged easily or even burst. Thereby the product's mechanical properties were reduced. Additionally, it was reported that metal oxides, organic acids, lead salt, zinc salt, and cadmium salt would activate AC, which could

effectively reduce the thermal decomposition temperature (Chen and Chen 2005). Therefore, the exothermic FA must be modified before it is used.
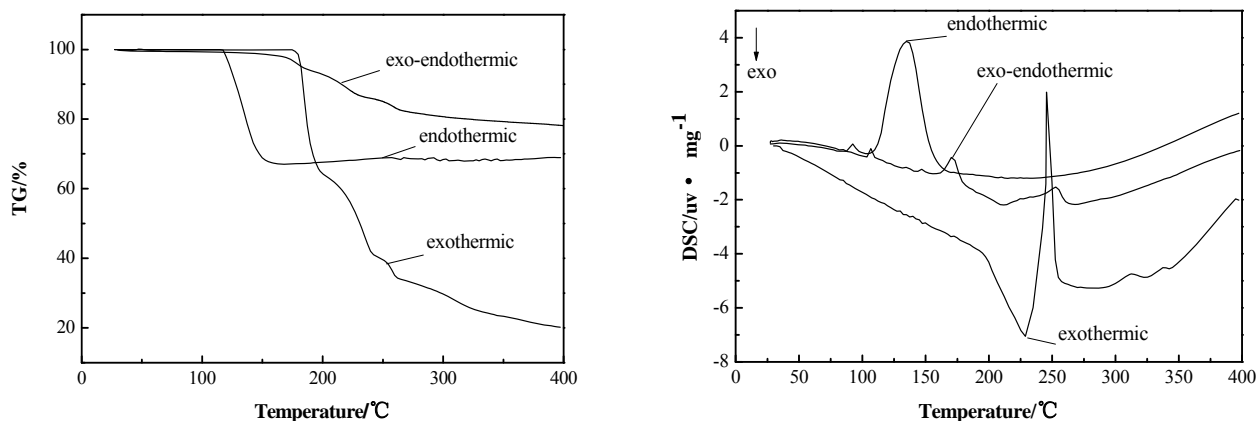

Fig. 1. Thermo-decomposition behaviors of three types CFAs. Left: TG, Right: DSC.

Thermal Properties of Modified Exothermic FA with Different Amounts of Modifier

ZnO (size 40 nm) and $Zn(St)_2$ complex (called 'modifier' for short) were used to modify AC. The thermal spectra of exothermic foaming agent with different amounts of modifier are pictured in Fig. 2. Modifier content of 5% meant $AC:ZnO:Zn(St)_2 = 100:5:5$.

The T_i gradually decreased with an increasing amount of modifier. Furthermore, with the increase in modifier content, the exothermic reaction temperature of AC decreased and the exothermic enthalpy increased. Meanwhile, the liberated N_2 and CO, which were generated from decomposition, could play a role in foaming. On the other hand, the endothermic reaction lagged and the endothermic enthalpy was reduced. When the modifier amount was 5%, 10%, and 20%, the T_i values were 182.1 °C, 177.2 °C, and 171.5 °C, respectively. It was obvious that the T_i of modified AC with addition of 10% and 20% modifier was much closer to the foaming temperature of the composite.
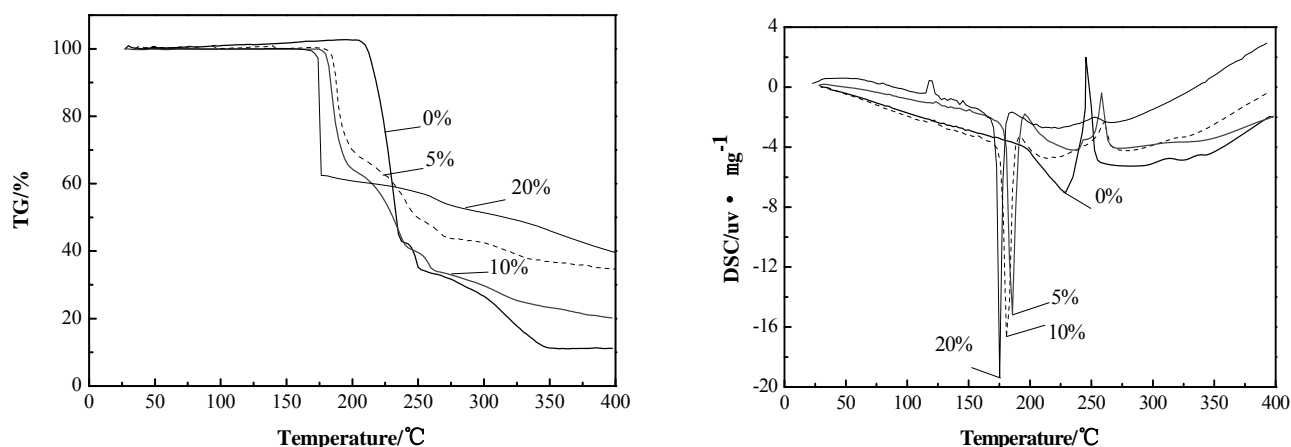

Fig. 2. Thermo-decomposition behavior of modified exothermic CFAs. Left: TG, Right: DSC

Effects of Modifier Content on Physico-mechanical Properties of Composites with Exothermic FA

Table 1 shows the influence of modifier content on the physico-mechanical properties of composites all containing 1% modified exothermic FA. When the modifier amount increased from 5% to 10%, the density of composite declined, mechanical properties were enhanced, and the VST increased slightly. When the content of modifier was 10%, the overall mechanical properties with respect to the bending performance and the specific tensile and notched impact strength reached maximum.

Table 1. Physico-mechanical Properties of Composites with 1% Exothermic FA

Modifier Content (%)	Density (g/cm^3)	Specific Flexural Strength (MPa)	Flexural Modulus (MPa)	Specific Tensile Strength (MPa)	Elongation At Break (%)	Specific Impact Strength (KJ·m^{-2})	VST (°C)
5	0.92± 0.004	41.80± 0.38	2704.02± 83.64	23.36± 0.13	4.46±0.18	6.73± 0.54	155.1 ±0.8
10	0.87± 0.003	46.20± 0.44	2807.39± 87.32	25.83± 0.03	4.94±0.23	7.72± 0.48	155.6 ±0.6
20	0.86± 0.004	44.17± 0.42	2615.73± 54.86	25.78± 0.09	4.41±0.16	7.81± 0.33	155.8 ±1.1

Note: Specific strengths were calculated from the ratio of strengths to their specific densities.

Based on a comprehensive consideration of the thermal decomposition temperature of foaming agent, the physico-mechanical properties and the cost of material, the most suitable amount of modifier was judged to be 10%.

Comparison of the Physico-mechanical Properties of Composites with Modified Exothermic FA and Exo-endothermic FA

Figure 3 shows the mechanical measurement of bamboo powder-PP foamed composites containing the modified exothermic FA and exo-endothermic FA. One can notice that a slight but significant improvement in density reduction and mechanical properties was achieved by utilizing a foaming agent for composite. The optimum amount of both exothermic and exo-endothermic FA was 1%. When adding 2% exothermic FA, the excess amount of AC agglomerated easily, owing to the electrostatic interaction. The incompletely decomposed AC may cause larger cells in the course of foaming, thus resulting in the reduction of mechanical properties. It was evident that the composite with 1% modified exothermic FA showed the lowest density and best mechanical properties. The density was reduced by 14.2% and decreased up to 0.87 g/cm^3. The specific flexural, tensile, and notched impact strengths reached maximum values of 46.20 MPa, 25.83 MPa, and 7.22 KJ/m^2, and the improvements were 16.8%, 20.5%, and 40.2%, respectively, compared to the non-foamed composite.

The VST data revealed that the values obtained were high enough to ensure use in several applications. Such foamed composites can be used in many industrial applications such as building materials, furniture, decorative plates, and automotive interior parts, and so on.
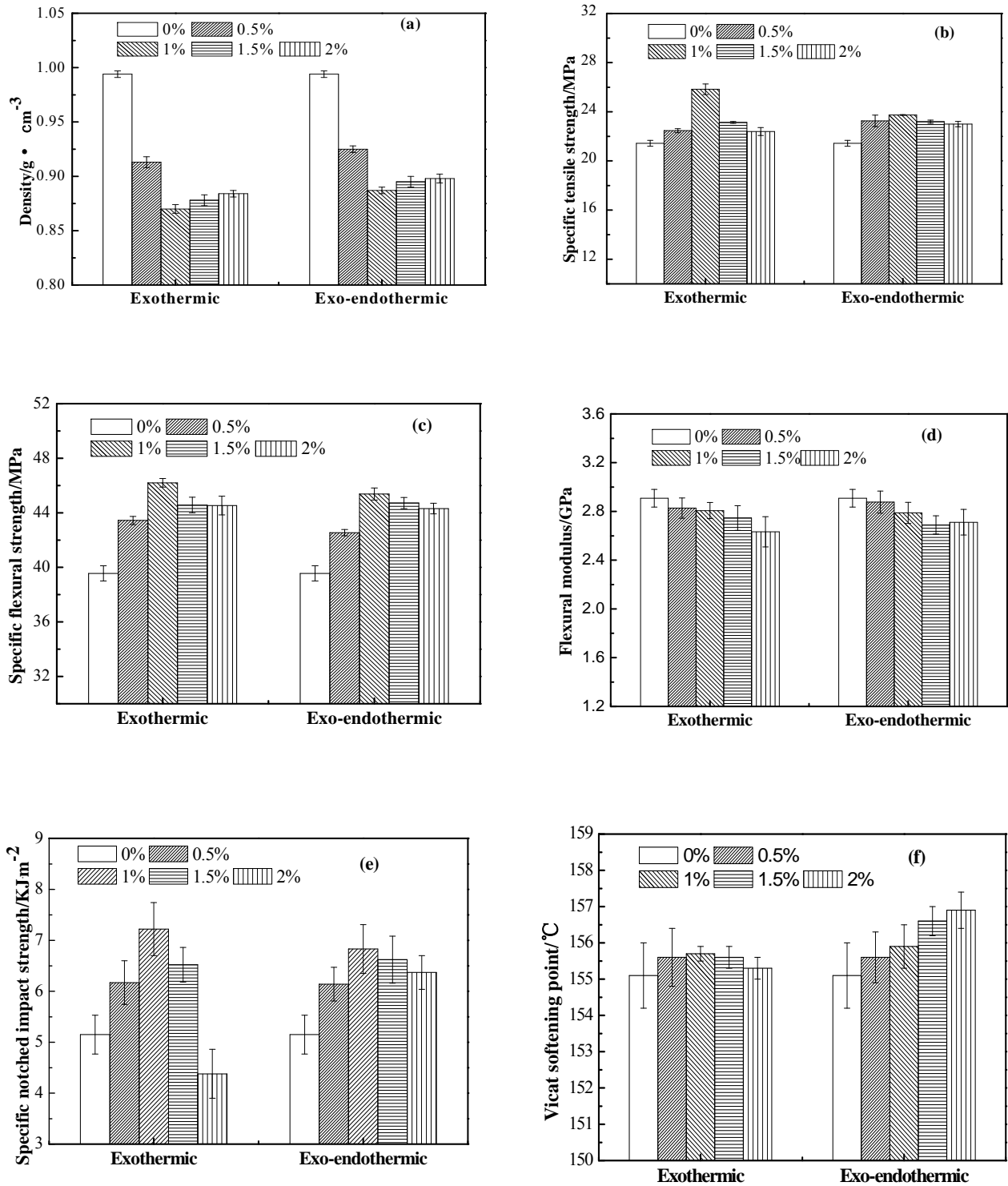
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Fig. 3. Influence of the CFAs on the physico-mechanical properties of foamed composites: (a) density, (b) specific tensile strength, (c) specific flexural strength, (d) flexural modulus, (e) specific notched impact strength, and (f) vicat softening point

Effect of CFAs on Cell Morphology

The cell morphology in the surface of fractured specimens was investigated by means of the ESEM, and results are presented in Fig. 4. CFAs played a significant role in the cell size and cell distribution. A larger cell size (around 65 to 219 μm) was observed from the composite containing 1% endothermic FA, and a smaller cell diameter (28 to 180 μm) was seen from the composite adding 1% exo-endothermic FA. The reason for the growth of some large irregular bubbles was that the generated gas migrated preferentially to the existing bubbles instead of nucleating new bubbles. In addition, the composite with 1% exothermic FA showed better cell distribution than those with the other FA. The difference in the cell morphology of foamed composites with various CFAs may result from the decomposition behavior of CFAs and the nature of gas given off upon their thermal decompositions (Fig. 1). When adding 2% modified exothermic FA, the cell dimension became larger and the diameter was 94 to 193 μm. Some unfragmented AC may yield bigger cells, and some bubbles merged and even ruptured. This caused stress concentration, resulting in reduction of mechanical strength. Based on the results of this work, it appears that the cell structure of the composite with a 1% exothermic FA showed the best performance.
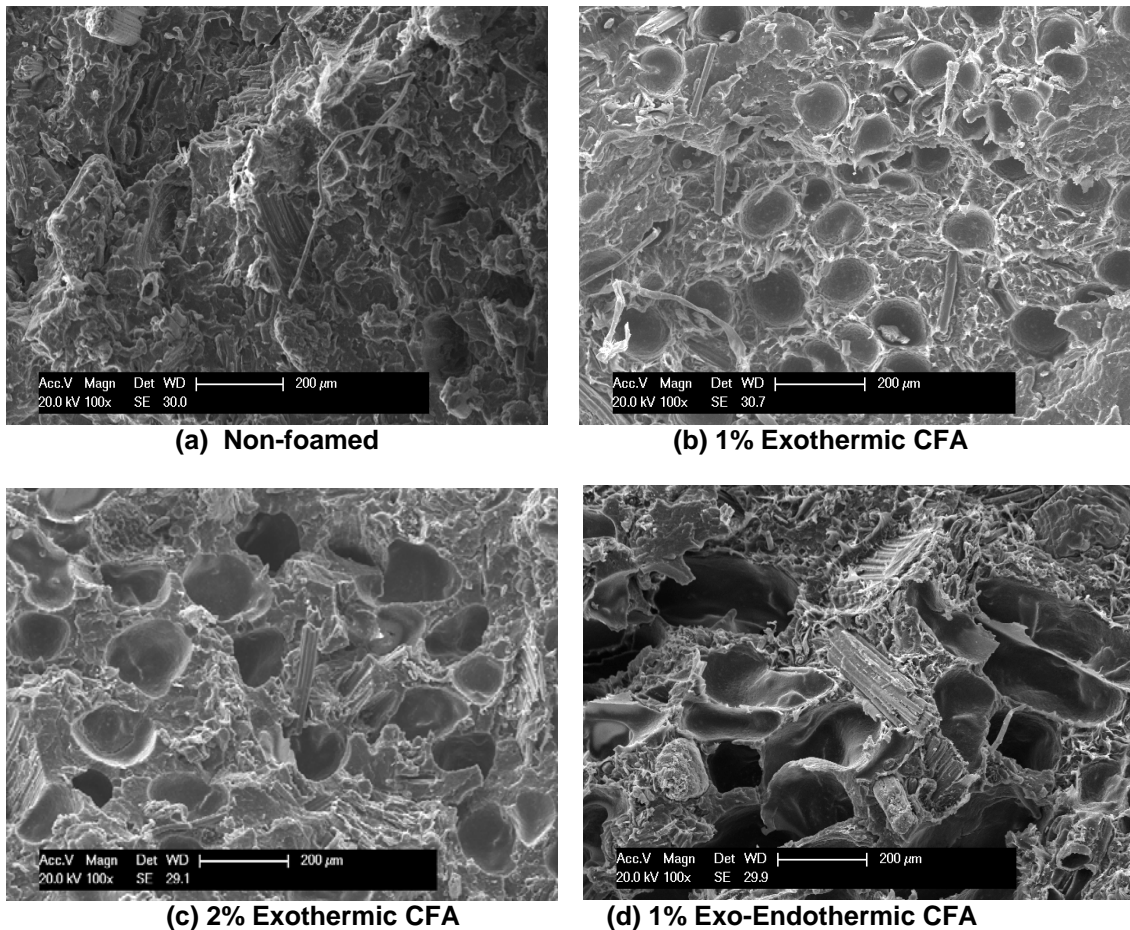

(a) Non-foamed

(b) 1% Exothermic CFA

(c) 2% Exothermic CFA

(d) 1% Exo-Endothermic CFA

Fig. 4. Cell structure of bamboo powder-PP foamed composites with CFAs

Rheological Behavior of Composites with Modified Exothermic FA

Strain sweep

In order to determine the upper limit of the input strain beyond which the system was in the nonlinear region, strain sweep experiments were firstly applied at a frequency of 0.1 Hz at 180 °C in the strain amplitude range of 10^{-4}% to 5% and were scanned from a small strain to a large strain. The changes of the storage modulus (G') and loss modulus (G'') with the strain (γ) in a logarithmic sweep mode are illustrated in Fig. 5. The composites with different contents of FA had nearly the same critical shear strain. When the strain was larger than 0.02%, G' and G'' dropped dramatically for all composites with the increase of the strain, and composites showed the "Payne effect" (Payne and Whitaker 1971). This effect is manifested as a dependence of the viscoelastic storage modulus on the amplitude of the applied strain. And at this moment the melt structure was destroyed, and the system showed a significant nonlinear behavior. The nonlinear viscoelastic behavior is related to entanglements between the polymer molecules or the melt fracture under the larger strain. Also, the change of modulus reflects changes of melt structure (Lion and Kardelky 2004). For the WPC systems with addition of 1% and 2% modified exothermic FA, there was an effective reduction in modulus compared to those of composite system without any FA. This may be due to the rigidity decreasing with addition of FA, and the FA could play a role as plasticizer when it reached a certain amount. This behavior suggested that a certain amount of FA had some effect on the microstructures of composites and improved the flowing behavior to some degree.
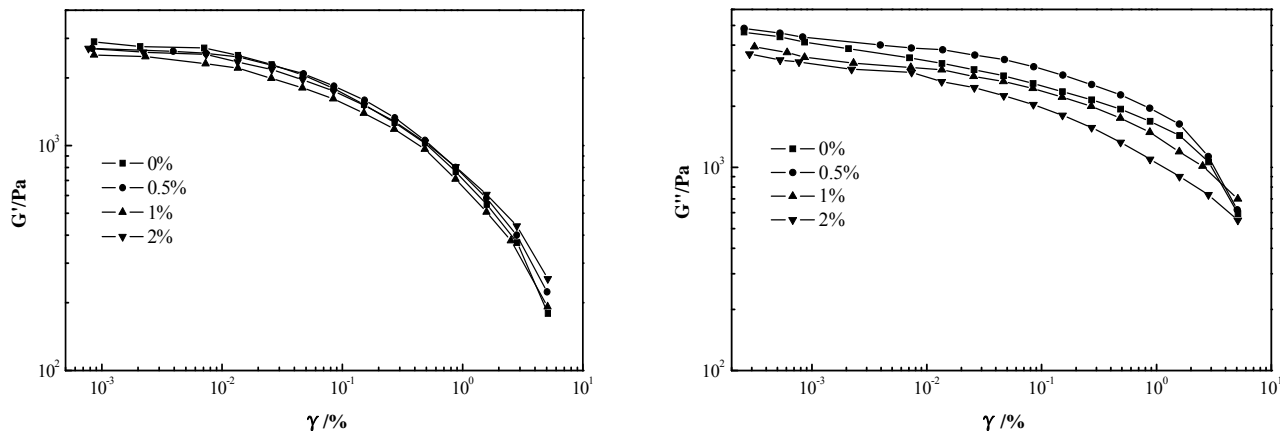

Fig. 5. The strain dependence of dynamic viscoelastic functions for composites with different exothermic CFA content at 180 °C

Frequency sweep

The dynamic viscoelastic measurements were done in the linear viscoelastic region at a constant temperature of 180 °C. The effects of adding different concentrations of modified exothermic FA (0%, 0.5%, 1%, and 2%) on the storage modulus (G') and loss modulus (G'') as a frequency (f) function are presented in Fig. 6 (a) and (b). From the charts it is possible to observe the "second plateau" phenomenon. G' and G'' tended to level in the low frequency region (Ferry 1980) and showed a significant increase with the increase of frequency. The viscoelastic response of bamboo powder/PP composites with

different contents of foaming agent varied. Compared to the non-foamed composite, the modulus was enhanced when adding 0.5% and 1% FA due to enhanced rigidity. The modulus was reduced when adding 2% FA, due to the decreased volume of solid polymer. According to the linear viscoelastic theory, the value of the slope of lgG'-1gω in the terminal zone (that is, the low-frequency zone) is 2. However, the multiphase/multicomponent polymer rheological results showed that the slope of the lgG'-lgω curve at the terminal region often deviated from the value 2 mentioned above, and the slope was closely related to the variation in the polydispersity of the composite. The degree of deviation from this theoretical value would be sensitive to the non-homogeneous degree of the macromolecule system (Zheng *et al*. 2004). Through linear fitting of the lgG'-lg$f$ curve in low frequency, the slopes of non-foamed sample and samples with 0.5%, 1%, and 2% FA were 0.591, 0.544, 0.561, and 0.549, respectively. The coefficients of determination were over 0.99. The available research showed that the higher the slope (as calculated using the above method) is, the greater the homogeneous phase the composite had (Zhou *et al*. 2007).   Therefore, the results illustrated that the degree of homogeneity of all composites was not high, and the decrease in the slopes of lgG'-lgω showed that the compatibility got a little worse after adding the FA.
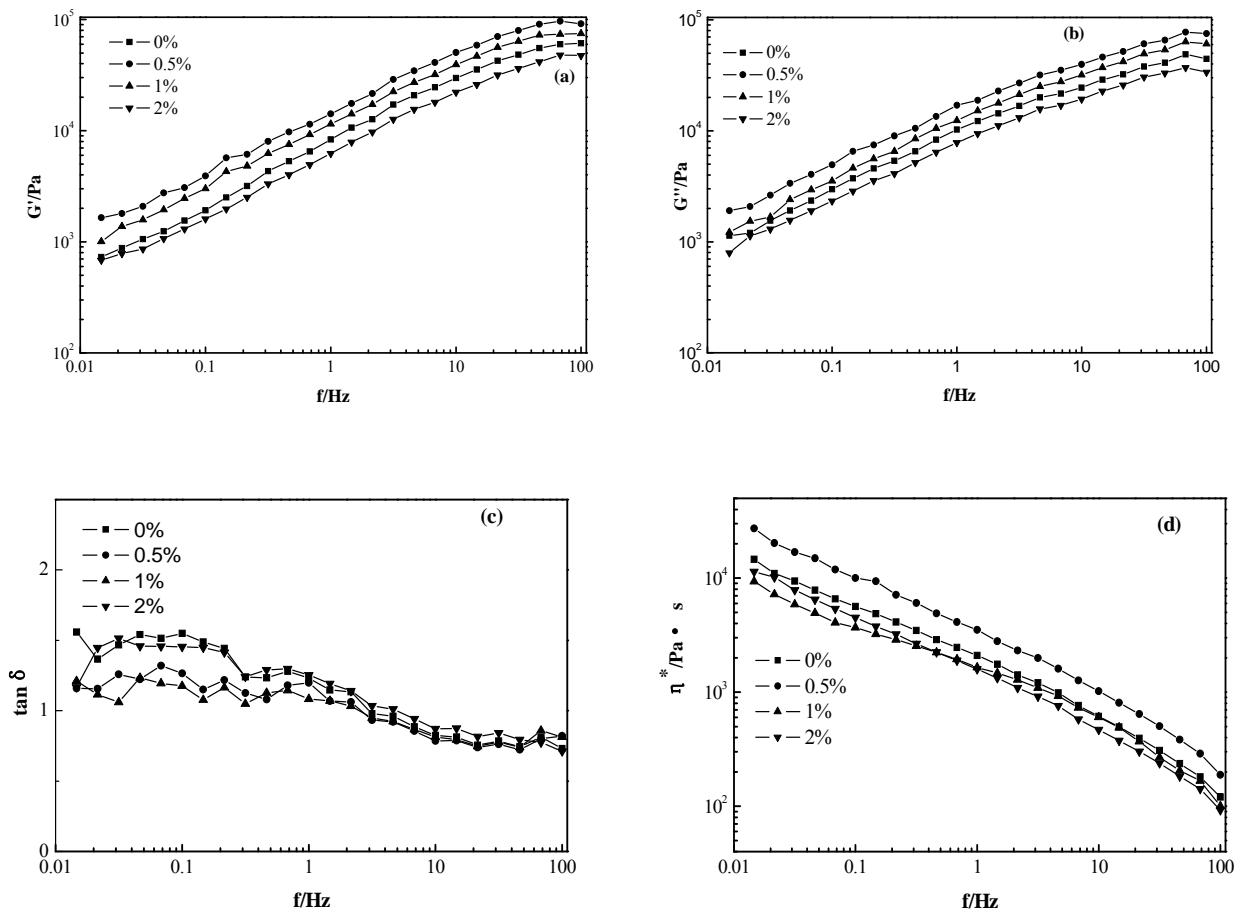

Fig. 6. The frequency dependence of dynamic viscoelastic functions for composites with different content of exothermic CFA at 180 °C

On the other hand, the loss tangent (tanδ) is sensitive to the changes of phase structure for polymer blends and can be used as a criterion for judging the presence of phase-segregated domains. The frequency (f) dependence of tanδ is presented in Fig. 6 (c). The same flattened section in the curves of Fig. 6 (c) indicated the presence of relaxation and degree of phase separation in the composites. In frequency ranges of about 0.1 to 6 Hz, it can be observed that both non-foamed and foamed composites showed liquid viscoelastic behavior ($G'' > G'$), which was otherwise in the range 6 to 100 Hz. Figure 6 (d) shows the complex viscosity (η^*) versus f for the samples with different percentages of FA. The η^* decreased substantially with an increase of f, and all samples showed shear thinning behavior. Compared to the non-foamed composite, a subtle reduction in complex viscosity was observed for composites with 1% and 2% FA. That is to say, the melt structure of composites with 1% and 2% FA was more easily destroyed, with a corresponding increase in the flowing behavior of the composites.

Shear rate sweep

Figures 7 (a) and (b) show the effects of the modified exothermic FA content on the shear rate ($\dot{\gamma}$) dependence of rheological behavior at 180 °C. It was apparent that all composites evolved from the Newtonian region to a non-Newtonian region. When $\dot{\gamma}$ was small, the $\dot{\gamma}$ dependence of apparent viscosity (η) was not apparent. When $\dot{\gamma}$ reached the critical shear rate of 10 s^{-1}, the value of η decreased with an increasing $\dot{\gamma}$, which showed typical shear thinning behavior. The impact of FA content on the flow curve was not obvious. The non-Newtonian fluid index (n) was used to characterize the degree of deviation of fluid from the Newtonian fluid. The n was calculated from the power-law equation

$$\tau = K\dot{\gamma}^n \tag{1}$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, K is the viscosity coefficient, and n is the non-Newtonian fluid index (Xiao *et al.* 2007). The value of n is the slope of the lnτ-ln$\dot{\gamma}$ curves, and is calculated easily. As seen in Fig. 7 (d1), the values of n were all less than 1, suggesting that composites belonged to the non-Newtonian pseudoplastic fluid category (Gu *et al.* 2003). When the FA content increased, the non-Newtonian fluid index increased, illustrating that the Newton behavior was enhanced. It was clearly seen that as FA content increased, on one hand, the macromolecular mobility of system was enhanced, and the fluidity increased, and on the other hand, the $\dot{\gamma}$ dependence of η was reduced and the processing conditions became more stable. Additionally, for pseudo-plastic fluid, when n was greater, the uniformity of mixing increased (Shi and Wu 2009).

Figure 7 (c) illustrates the η-$\dot{\gamma}$ flow curves of bamboo powder/PP foamed composite with 1% modified exothermic FA at different temperatures. At the same shear rate, when the temperature increased from 160 °C to 170 °C, the value of η decreased only slightly. It was evident that the effects of temperature from 170 °C to 190 °C on the flow behavior were significant, the flow curves descended, and the value of η showed a tendency to decline with increasing temperature. At given shear rate conditions, when the temperature increased, the capacity of macromolecular motion was enhanced. The

entanglement between the molecules was reduced and the flow behavior was improved, so that the apparent viscosity in the flow curves was reduced. Furthermore, Fig. 7 (d2) shows that with increasing temperature, the non-Newtonian fluid index increased; thus the shear rate dependence of apparent viscosity at higher temperature got smaller. As can be seen from the above-mentioned results, processing technology should be strictly controlled. And when mixing, the mixture should be first mixed at a low temperature with a low speed, and then gradually mixed at a high temperature with a high speed.
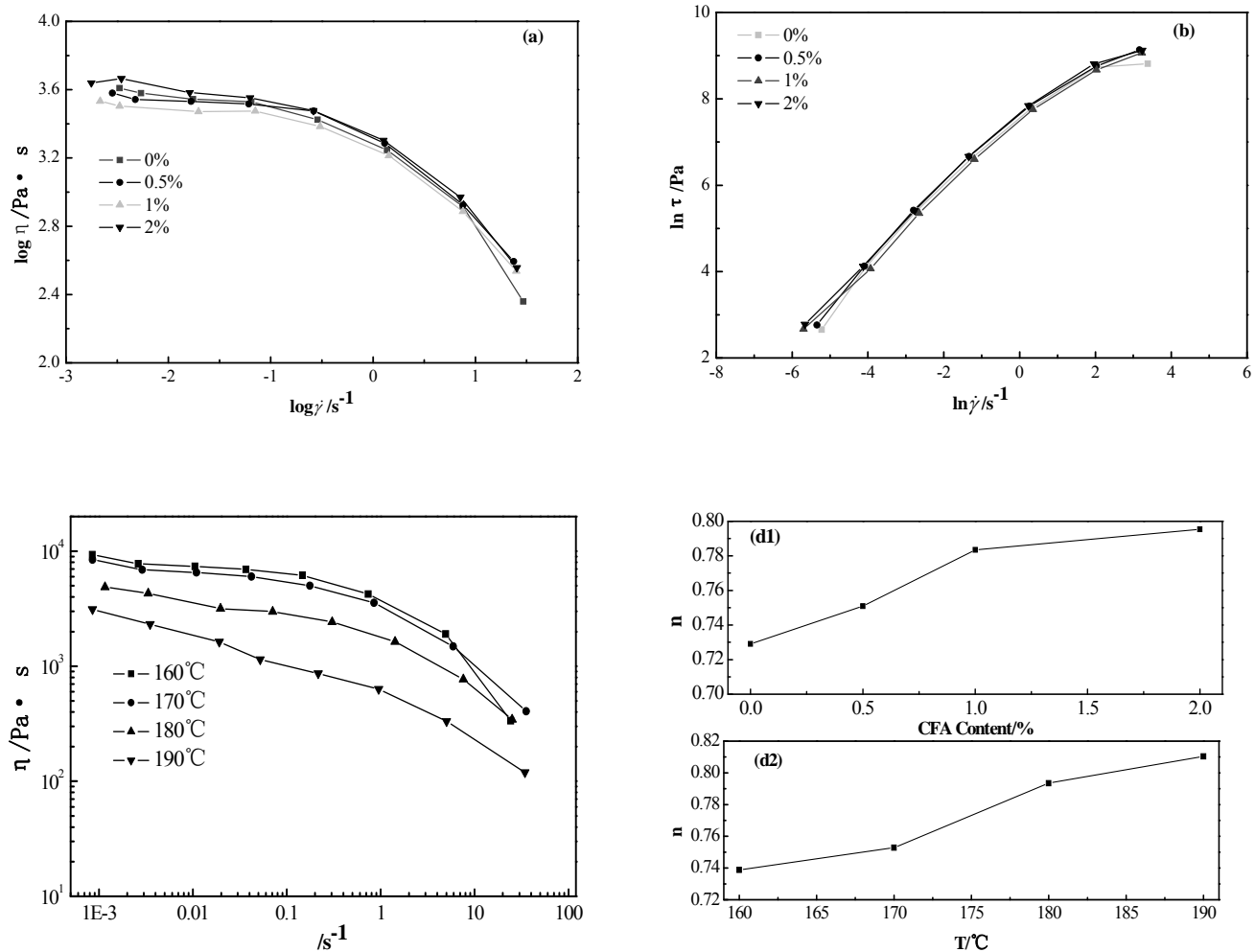

Fig. 7. The shear rate dependence of dynamic viscoelastic functions for composites with different content of exothermic CFA at 180 °C.

Temperature sweep

To further investigate the relationship between rheological behavior and temperature of composites, the storage modulus (G') data were investigated, and the activation energy of viscosity flow (E) was calculated by temperature (T) scanning. The effects of FA content on the T dependence of G' were identified in Fig. 8. As the temperature increased, the storage modulus decreased. This was due to the fact that the

motion capacity of macromolecules was strengthened when the polymer was at a high temperature. Especially with the addition of 1% FA, the storage modulus decreased to a minimum. When the temperature exceeded 180°C, the Brownian motion of molecules became fast enough to get rid of the force between polymer chains and formed disordered polymer chains; thus the rheology curve of composite became close to a straight line. Furthermore, when the temperature was higher than the melting point of samples, the relationship of the apparent viscosity (η) and the temperature (T) was in agreement with the Arrhenius equation, that is (Al-Rawahi and Tryggvason 2002),

$$\ln \eta = \ln A + \Delta E_\eta / RT \tag{2}$$

where A is a constant representing the characteristics and relative molecular mass of polymer in the specific shear stress, R is the gas constant, T is absolute temperature, and E is the activation energy of viscous flow. According to the Arrhenius equation, the E value of the composite could be calculated, and it is given in Table 3. The viscous activation energy of bamboo powder/PP composite was found to be 42.63 KJ·mol^{-1}, and with the addition of 1% FA, the value of E reached a maximum (46.41 KJ·mol^{-1}). The higher value of E indicated that the apparent viscosity was more sensitive to the temperature. When processing this specimen, attention should be paid to controlling the processing temperature.
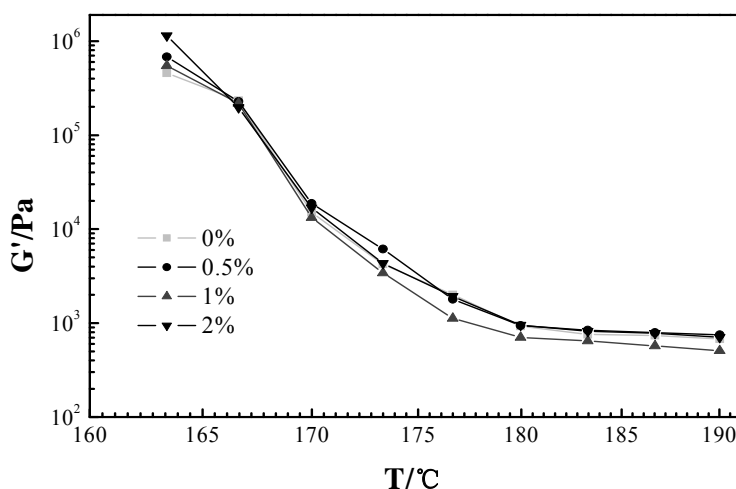

Fig. 8. The temperature dependence of dynamic viscoelastic functions.

Table 3. The Viscous Activation Energy of Composites

FA content (%)	E (KJ·mol^{-1})	R^2
0	42.63	0.9961
0.5	39.75	0.9688
1	46.41	0.9903
2	41.18	0.9780

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CONCLUSIONS

1. The 33 wt% bamboo powder/PP foamed composite with the modified exothermic FA showed better physico-mechanical properties and cell structure than that with exo-endothermic FA.
2. The optimum amount of both exothermic and exo-endothermic FA was 1%. With the addition of 1% modified exothermic FA, the density of foamed composite decreased by 14.2% and the mechanical strengths increased by 16.8% to 40.2% compared with the non-foamed composite.
3. The rotation rheological results indicated that the composites exhibited the "Payne effect" and the critical shear strain was 0.02%. Frequency scan results showed that the modulus decreased with 1% and 2% modified exothermic FA and the flowing behavior of foamed composites improved. When adding FA, the slopes of plotting lgG' versus lg$f$ in the low f region (terminal range) was slightly reduced, which indicated that the homogeneity of the composite decreased. The slope of the non-foamed composite was 0.591, and it was reduced to 0.561 for the composites containing 1% FA. The shear rate sweep results indicated that the composites showed typical non-Newtonian pseudoplastic fluid behavior, and the non-Newtonian fluid index increased with the increase of FA amount. The activation energy of viscous flow of the composite with 1% modified exothermic FA was 46.41 KJ·mol^{-1} with an 8.9% increase compared with the non-foamed composite.

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REFERENCES CITED

Al-Rawahi, N. Z., and Tryggvason, G. (2002). "Numerical simulation of dendritic solidification with convection：Two-dimensional geometry," *Journal of Computational Physics* 180, 471-496.

Bledzki, A. K., and Omar, F. (2006a). "Microcellular injection molded wood fiber-PP composites: Part I - Effect of chemical foaming agent content on cell morphology and physico-mechanical properties," *Journal of Cellular Plastics* 42(1), 63-76.

Bledzki, A. K., and Omar, F. (2006b). "Microcellular injection molded wood fiber-PP composites: Part II - Effect of wood fiber length and content on cell morphology and physico-mechanical properties," *Journal of Cellular Plastics* 42(1), 77-88.

Bledzki, A. K., and Omar, F. (2005). "Effects of the chemical foaming agents, injection, parameters, and melt-flow index on the microstructure and mechanical properties of microcellular injection-molded wood-fiber/polypropylene composites," *Journal of Applied Polymer Science* 97, 1092-1094.

Bledzki, A. K., Zhang, W. Y., and Omar, F. (2005). "Microfoaming of flax and wood fibre reinforced polypropylene composites," *European Journal of Wood and Wood Products* 63(1), 30-37.

Chen L. J., and Chen H. Q. (2005). "Study on the active substances effect on the property of AC blowing agent and their activated mechanism," *Insulation Material* 1, 31-32.

Clemons, C. (2002). "Wood-plastic composites in the United States- The interfacing of two industries," *Forest Prod. J.* 52, 10-18.

Faruk, O., Bledzki, A. K., and Matuana, L. M. (2007). "Microcellular foamed wood-plastic composites by different processes: A review," *Macromolecular Materials and Engineering* 292(2), 113-127.

Ferry, J. D. (1980). *Viscolelastic Properties of Polymers*, John Wiley & Sons, Inc., New York.

Gu, F., Wang, S. F., Song, C. F., Lü, M. K., Qi, Y. X., Zhou, G. J., Xu, D., and Yuan, D. R. (2003). "Synthesis and luminescence properties of SnO_2 nanoparticles," *Chem. Phys. Letters* 372, 451.

Lakkad, S. C., and Patel, J. M. (1980). "Mechanical properties of bamboo: A new natural composite," *Fiber Science &Technology* 14, 319-322.

Lee, Y. H. (2008). "Foaming of wood flour/polyolefin/layered silicate composites," Ph.D Thesis, University of Toronto

Lion, A., and Kardelky, C. (2004). "The payne effect in finite viscoelasticity," *Inter. Jour. Plast.* 20, 1313-1345.

Matuana, L. M., Park, C. B., and Balatinecz, J. J. (1997). "Processing and cell morphology relationships for microcellular foamed PVC/wood-fiber composites," *Poly. Eng. Sci.* 37(7), 1137-1147.

Matuana, L. M., Park, C. B., and Balatinecz, J. J. (1998). "Cell morphology, and property relationships of microcellular foamed PVC-wood fiber composites," *Poly. Eng. Sci.* 38(11), 1862-1872.

Nawadon P., and Sirijutaratana C. (2011). "Influences of particle sizes and contents of chemical blowing agents on foaming wood plastic composites prepared from poly(vinyl chloride) and rice hull," *Materials and Design* 32, 2844-2850.

Payne, A. R., and Whitaker, R. E. (1971). "Low strain dynamic properties of filled rubbers," *Rubber Chem. Technol.* 44, 440-479.

Rachtanapun, P. S., Selke, E. M., and Matuana, L. M. (2003). "Microcellular foam of polymer blends of HDPE/PP and their composites with wood fiber*," Journal of Applied Polymer Science* 88, 2842-2850.

Rizvi, G. M., Park, C. B., and Matuana, L. M. (2000). "Foaming of PS/wood fiber composites using moisture as a blowing agent," *Polymer Engineering Science* 40(10), 2124-2132.

Shi, T. J., and Wu, D. F. (2009). *Polymer Rheology Base*, Chemical Industry Press, Beijing, China, 49-51.

Xiao, K. Q., Zhang, I. C., and Zarudi, I. (2007). "Mechanical and rheological properties of carbon nanotube-reinforced polyethylene composites," *Composites Science and Technology* 67(2), 177.

Zheng Q., Cao Y., and Du M. (2004). "Dynamic rheological behavior of polypropylene filled with ultra-fine powdered rubber particles," *Chinese Journal of Polymer Sci.* 22(4), 363-367.

Zhang, S. W., Rodrigue, D., and Riedl, B. (2005). "Preparation and morphology of polypropylene/wood flour composite foams via extrusion," *Polymer Composites* 26, 731-738.

Zheng, D. D., Liu, Y. H., and Lin X. Y. (2005). "Development and utilization of bamboo waste," *Fujian Forest Science* 32, 153-154.

Zhou, C. X. (2005). *Polymer Rheology Experiment and its Application*, Shanghai Jiaotong University Press, Shanghai, China.

Zhou, M., Song, Y. H., Sun, J., He, L., Tan, H., and Zheng, Q. (2007). "Effect of silane coupling agents on dynamic rheological properties for unvulcanized SSBR/silica compounds," *Acta Polymerica Sinica* 42(13), 5743-5747.

Zhou X. X., Lin Q. J., and Chen L. H. (2011). "Mechanical properties and rheological behavior of injection moulded foaming bamboo powder–polypropylene composites," *Advanced Materials Research* 287-290, 1980-1986.