Polym. Bull. (2011) 66:683–701
DOI 10.1007/s00289-010-0382-y

ORIGINAL PAPER

Dynamic rheological properties of wood polymer composites: from linear to nonlinear behaviors

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Received: 23 May 2010 / Revised: 2 August 2010 / Accepted: 15 September 2010 /

Abstract The microstructure of wood plastic composite (WPC) with respect to wood particle content and maleic anhydride-grafted polypropylene (MAHPP) compatibilizer is studied by both linear and nonlinear rheological methods in this article. The complete long characteristic relaxation behavior in linear region, which is closely related to the structure of wood particle aggregates and MAHPP compatibilizing effect at the interface, is limited by observing time. Fortunately, the Fourier transform rheology (FTR) by the stress control mode is found to be an effective method for further investigating the structure with long relaxation time in WPC system. The plateau value of I_{31} at high stress and the range of ϕ_{31} are proved to be corresponding to the content of wood particle agglomerates in the WPC melts and the type of interfacial hydrodynamic interaction. The interesting outcomes suggest that MAHPP do has the effect on changing the properties of the heterogeneous interface and confirm the difference of the structure with long relaxation time in WPC can be easily captured by the high sensitive FTR indeed.

Keywords Wood plastic composite · Dynamic viscoelasticity · Fourier transform rheology · Compatibilization

Introduction

Wood plastic composite (WPC) is an intimate mixture of wood and polymers, processed by techniques similar to the plastics industry. The main advantages of wood flours as filler are their low cost and abundant availability, renewability, biodegradability, and tailoring ability on the performance of polymers to meet various

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applications [1–4]. Among the influence factors such as wood type, particle size distribution, particle concentration and the type of polymer, the interaction between wood particles and polymer molecules at the interface is the principal factor that affects macroscopic properties of WPC [4–10]. It is the natural incompatibility between the polar hydrophilic wood flour and the nonpolar hydrophobic polyolefin matrix that usually leads to poor processability and weak mechanical properties of the products, which makes it necessary to add some suitable compatibilizers during the melt processing of the composites. At present, the maleic anhydride-grafted polyolefin has received much attention and becomes widely used because of its effectiveness in enhancing the mechanical performance, reducing the pathways for moisture absorption and reinforcing the resistance to microbial attacks [9–11]. Those improvements of the macroscopic performance are strongly related to the enhancement of the compatibility present at the interface between the wood particles and polymer molecules.

In a great number of studies, the mechanical properties are used to evaluate the interfacial compatibility between the matrix and wood particles. In fact, the mechanical properties of a WPC depend on many factors. The crystallinity and the crystal form of polyolefin, the shape, size, and agglomeration of wood particles, and the interactions between wood particles and the polymers play important roles in mechanical strength [11–15]. Compatibilizers should affect the crystallization of polymer and the dispersion of wood particles. This makes it improper to evaluate the wood particle–polymer interaction directly from mechanical properties. It is then desirable to characterize the particle–polymer interaction in melt state, where rheology becomes an effective tool. Although the rheology has been used efficiently to characterize the interfacial properties in the immiscible blends [4, 16, 17], few studies can be found to systematically analyze the effects of the compatibilizers on the rheological behavior of WPC.

The introduction of wood particles into polyolefin leads to a clear change in the rheological properties of the WPC melts from liquid-like to solid-like [3, 18, 19]. Studies on the rheological properties of WPC in simple shear flow are inclined to provide an insight into the industrial extrusion response of the composites [1, 18, 19]. Capillary rheometer is often used to simulate the extrusion of WPC. The shear flow in capillary dies exhibits surface tearing phenomenon particularly for the high wood particle filled system of wood composites at low shear rate [18]. The lubrication contributions of MAHPP are proved by the Mooney analysis [19]. Due to the easier migration of wood particle from wall to centre in capillary rheometer, the higher wall slip velocity is observed for the WPC with MAHPP additive at the same shear stress than that in the system without compatibilizers [8, 19]. Although apparent shear viscosity increases with the wood content, the MAHPP compatibilization effect seems to be weaken by the shear-thinning behavior of the WPC melt, and the difference in the viscosity at high shear rates is obscure[1]. This suggests that the variation of shear viscosity might not be a good indication of the compatibilization effect of MAHPP.

Compared with the simple shear flow applied by the capillary rheometer, the use of oscillatory flow in linear region has been recommended to study the microstructures of the WPC, since dynamic experimental can provide both elastic and viscous properties which are closely relative to wood particle dispersion and the interface character between the wood and polymer matrix [2, 8]. Small amount of maleated polyolefin can obviously decrease the storage modulus especially in the high wood particle loading system, but the compatibilizer effect at lower wood content seems to be not obvious in small amplitude oscillatory flow [3]. However, there are enough evidences that maleated polyolefin does improve adhesion between the wood particles and polymer matrix even at lower filler content [9, 13, 20]. Furthermore, the frequency scaling of the dynamic viscoelastic properties of WPC with the different wood particle loadings shows the same relaxation behavior as the pure polyolefin, which indicates that longer relaxation process of the interface is difficult to probe in short time by the common frequency sweep in linear region [3].

As a matter of fact, the WPC melt is typically a noncolloidal suspension of coarse particles in a non-Newtonian fluid, which may exhibit remarkable nonlinear properties even at very small deformation [2, 3]. In such cases, it is possible to use the higher strain/stress level to study the corresponding strain/stress response, from which the structure changes under different strains or stresses can be used to investigate the effect of compatibilizers. However, typical analysis based on the storage modulus and loss modulus is not sufficient since both of them lose the meaning as in linear viscoelastic region [21, 22]. Therefore, it is necessary to perform FTR for the nonlinear behavior of WPC melt.

In this article, the rheological properties of quite complex WPC system as the functions of the filler content as well as the maleated polyolefin compatibilizers will be studied from linear region to the nonlinear region. First, small amplitude oscillation shear is used as the normal technique to find out the structure difference caused by the compatibilizers. Then the structure evolution process of the WPC in nonlinear region is carried out as the stress amplitude increases. Taking into account the linear and nonlinear rheological properties in all, large-scale relaxation behaviors in WPC and the character of the interfacial hydrodynamic interaction are discussed in details.

Linear and nonlinear oscillatory shear

The oscillatory shear flow is often applied to study the linear and nonlinear rheological behavior of complex fluids [21–25]. The dynamic oscillation can avoid the flow instability to a bare minimum, particularly for high solid-filled system, which is the basis to obtain the reliable and reproducible rheological data. Either stress control mode or strain control mode can be used for oscillatory experimental [23, 26]. In case of stress control mode, we can describe the input harmonic shear stress signal as:

$$\sigma(t) = \sigma_0 e^{i\omega t} \tag{1}$$

where σ_0 is the stress amplitude and ω is the imposed frequency.

When the input shear stress is small enough, the microstructure of materials is closely to be in the static state. This is known as the linear viscoelastic region, where the strain response is regardless of the applied stress amplitude. In small amplitude oscillatory shear, the response signal is still a single harmonic function but with a phase shift and can be expressed as

$$\gamma(t) = \gamma_1 e^{i(\omega t+\delta_1)} \tag{2}$$

where the response frequency ω exclusively equals to the excitation frequency for the shear stress $\sigma(t)$. γ_1 is the amplitude of shear strain, and δ_1 is the phase angle. In the linear region, the storage modulus G' and loss modulus G'' are defined as

$$G' = \frac{\sigma_0}{\gamma_1}\cos\delta_1 \tag{3}$$

$$G'' = \frac{\sigma_0}{\gamma_1}\sin\delta_1 \tag{4}$$

The appearance of linear viscoelastic properties lies on the multi-scale relaxation behaviors where the frequency of oscillatory can be used as a probe to find out the relaxation process at specific time scale. In other words, if we want to observe the much longer characteristic relaxation behavior, it is necessary to use lower frequency and spend more time [22, 27]. However, the structure with long relaxation time in WPC system can be excited by a large stress which is out of the linear region, i.e., when the input shear rate exceeds the inverse of the longest relaxation time of the system, the large-scale structure can be investigated in nonlinear region. As the oscillatory stress goes out of the linear region, the output signal will distort from a pure sinusoidal wave form corresponding to the nonlinear behavior. Usually the nonharmonic output signal can be well presented by the Fourier series as:

$$\gamma(t) = \sum_{k=1}^{\infty}\gamma_k(\sigma_0,\omega)e^{i(k\omega t+\delta_k)} \tag{5}$$

It is clear that the strain amplitude becomes dependent on the stress amplitude and the frequency as well. Such expression is the foundation of FTR, which suggests that Fourier transform procedure can be used to determine the amplitude and the phase angle of higher harmonics. The degree of nonlinearity can be evaluated by the relative intensities of nth harmonics to that of the first one, i.e., $I_{n1} = \gamma_n/\gamma_1$. A relative phase angle can also be defined as:

$$\phi_{n1} = \delta_n - n\delta_1 \tag{6}$$

Although higher harmonics can be observed in experiments, in many cases, the analysis of nonlinear oscillatory data is often focused on the relative amplitude intensities I_{31} and phase shift angle ϕ_{31} with respect to the third harmonic and the fundamental frequency, which are believed to be important to study the relation between the structures of materials and nonlinear properties [22–25, 28–34].

Experimental

Materials and methods

Wood flour, a byproduct in furniture manufacturing, is supplied by Linan Mingzhu Bamboo and Wood Powder Company, China. Only particles that pass through a

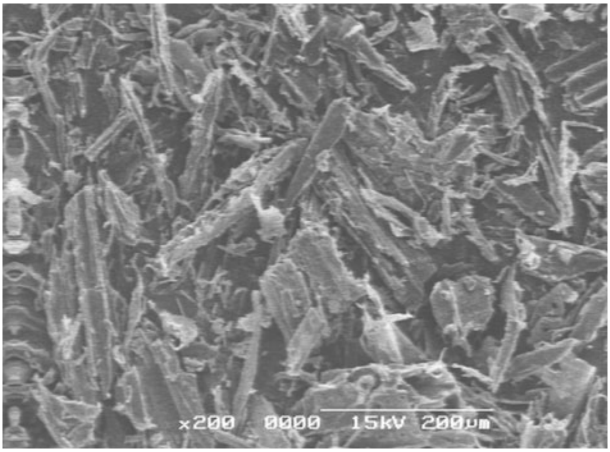


Fig. 1 Scanning electron micrograph of the wood particles

sieve of mesh 80 (187 μm) were used in this study. Figure 1 shows a scanning electron micrograph of the wood particles revealing that the particles are not exactly short fiber shaped and the average particle sizes are below 187°μm. The polymeric materials used in this study are isotactic polypropylene particle (Y1600, Sinopec Shanghai Petrochemical Corp., China) with the degree of isotacticity about 96%, the weight-average molecular weight ($\overline{M_w}$) about 660,000 g/mol, and the number-average molecular weight ($\overline{M_n}$) about 80,000 g/mol. The commercial maleic anhydride-grafted polypropylene (MAHPP, CMG9801) with ultra-high liquidity (melt flow index (MFI) > 80 g/10 min, at 2.16 kg and 190 °C) and high grafted ratio (1 g MAH/100 g PP) is supplied by Shanghai Sunny New Technology Development Co., China. Before blending process, the wood flours are drying at 90 °C for 2 h and heating at 105 °C for another 1 h under vacuum condition to minimize the moisture content. The PP particles are stabilized by addition of 1 wt% Irganox 1010 (Ciba, Switzerland) antioxidants to prevent the degradation of PP during the rheological measurement at 190 °C. Mixtures of PP and wood flours, containing 30, 40, or 50 wt% of wood flours, respectively, are melting compounded by a Haake Rheocord 90 mixer at 180 °C with a roller speed of 90 rpm. Finally, the composites are pressed into some 3 mm thick disc-shaped specimens by compression-molding at 180 °C for 10 min overall compression time. The detailed compositions of samples used in this study are listed in Table 1.

Scanning electron microscopy (SEM)

The WPC is fractured under liquid nitrogen and the cross section is previously coated with gold. A scanning electron microscopy (model SEM S-2150, Hitachi, Japan) is used to study the morphological structures of the composite.

Rheological measurement

A rotational rheometer (Gemini 200HR, Malvern Instruments, UK), equipped with a serrated plate geometry (25 mm in diameter), is used for both linear and nonlinear viscoelastic experiments in dynamic oscillatory mode, both of which are under stress-controlled conditions. This parallel geometry is advantageous for particle suspensions measurements since the gap can be set to be larger than the particle size. With higher wood flour loading, it becomes increasingly difficult to obtain the reliable and reproducible data. One main reason for this problem is the natural thixotropic properties of the WPC system, as emphasized repetitiously in the former references [2, 3], in which the microstructure is very sensitive to the shear history and it is seems to be difficult to get the identical initial state. Taking into account these adverse characteristics of WPC system, a careful sample preparation method was carried out before every rheological testing for each sample. The test sample of about the 3 mm thickness and 30 mm diameter was put between the plates and heated to 190 °C for 3 min. After adjusting the gap to 2.2 mm, the squeezed molten composite was carefully trimmed off for attaining smooth edge surface. This distance allowed the ratio of gap to fiber size to be larger than 10. Prior to every rheological test, the molten sample was equilibrated for 5 min to erase any previous thermal and deformation history that possibly affected the subsequent dynamic tests. In addition, the total time of one testing processing was strictly restricted in 35 min, in order to reduce the effect of wood thermal degradation on the rheological behaviors of the WPC.

Isothermal dynamic frequency sweep (100–0.01 rad/s) experiments were performed at a given stress amplitude in linear region at 190 °C. To investigate the nonlinear rheological properties in large amplitude oscillatory shear flow, the nonlinear dynamic experiments in different shear stress range were performed at a fixed oscillatory frequency of 1 Hz. After 60 cycles of each applied stress, the strain responses were recorded for eight periods with 8,192 sampling points.

Table 1 The composition and the symbol of the sample prepared in this research

Sample	Wood content (%)	MAHPP content (%)
PP	0	0
W30	30	0
W40	40	0
W50	50	0
W30MA5	30	5
W40MA5	40	5
W50MA3	50	3
W50MA5	50	5

Results and discussions

Linear viscoelasticity

The frequency dependences of G' and G'' in linear region for the pure PP and WPC are shown in Fig. 2. The stress amplitude is 20 Pa, which lies in the linear region according to the stress amplitude sweep (see below). As seen in this figure, the pure PP exhibits the typical terminal behavior of linear polymer at low frequencies, i.e., $G' \propto \omega^2$ and $G'' \propto \omega$, which is attributed to terminal relaxation of PP molecules [35]. The dynamic moduli of WPC increase with the wood loading and no terminal relaxation can be observed. Such nonterminal behavior suggests the relaxation process of structures will happen at even lower frequency (or equivalently taking longer time). The longer relaxation time in WPC is possibly related to the particle–particle interactions and particle–polymer interactions [8, 36]. Moreover, the effect of MAHPP in WPC system is quite obvious for W50MA5 which leads to an effective decrease in the apparent dynamic modulus, but there is no apparent difference in moduli of W30MA5 compared those of WPC sample without compatibilizer. Similar dependency of MAHPP on wood content was also reported by Marcovich et al. [3]. This behavior suggests that the compatibilizer has certain effect on the microstructures of composites. However, linear viscoelasticity might be insufficient to characterize the change of structures especially at low wood concentrations.

It is believed that the MAHPP modifiers can really change the interface properties in the incompatible blends, which can be directly proved by the observation on the phase structures. Figure 3 shows the SEM images of the fractured surfaces for the WPC samples. For composites without MAHPP, the interface between the PP matrix

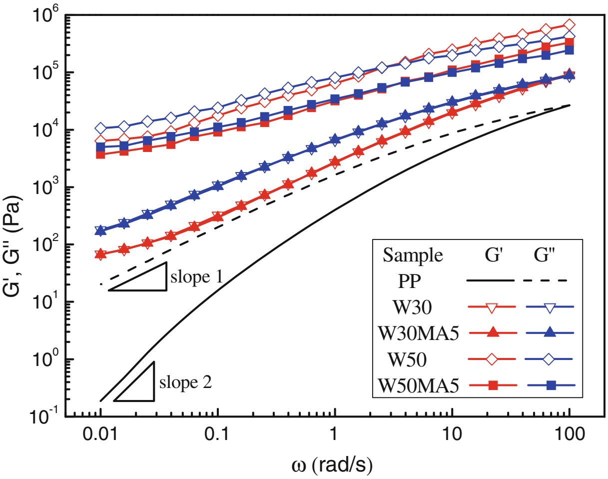


Fig. 2 Frequency sweep of WPC in the linear viscoelastic region at 190 °C with different contents of wood particles and with or without MAHPP compatibilizer

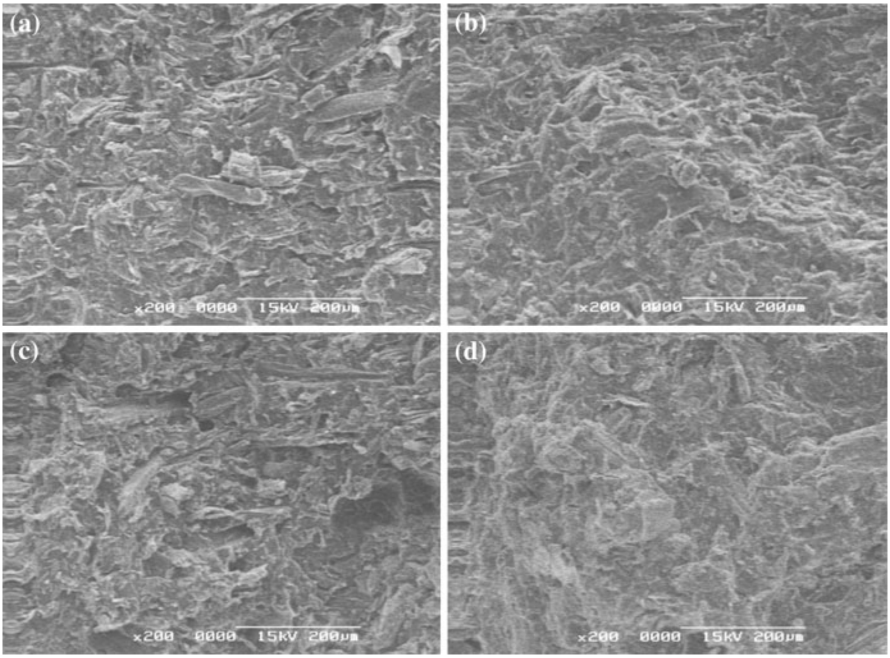


Fig. 3 Scanning electron micrographs of the fractured surfaces of WPC: **a** W30, **b** W30MA5, **c** W50, and **d** W50MA5

and wood particle is clearly showed in Fig. 3a and c, respectively. However, the boundary of wood particle becomes indistinct for composites with MAHPP (Fig. 3b, d), which implies MAHPP improves the compatibility between polymer matrix and wood particles. This is consistent with previous studies that the adhesion between the two phases is strongly enhanced when MAHPP is added [37]. The SEM results confirmed that the MAHPP used in our experimental has a strong compatibilizing effect indeed in the interface layer between the wood particle and PP in the composites with wood particle content of both 30 and 50 wt%.

To further investigate the relaxation behavior of pure PP and WPC, the relaxation spectrum was calculated from storage modulus G' and loss modulus G'' data by GENEREG program [35, 38] (as shown in Fig. 4). The weighted relaxation spectra show that the pure PP only has one characteristic relaxation time ($\lambda_M \approx 0.16$ s), which is related to the relaxation process of linear molecules [35]. The relaxation processes of the PP matrix in WPC samples are slightly slower as the wood content increases. This suggests that the relaxation mechanism of PP matrix in WPC samples is barely influenced by the addition of wood particles.

Furthermore, for WPC samples with or without MAHPP compatibilizer, they showed an additional longer characteristic relaxation process other than that of linear PP molecule in matrix, although the longer relaxation process cannot be captured completely in Fig. 4 due to the limited frequency range. This indicates that there is an additional longer characteristic relaxation process in the WPC, which can

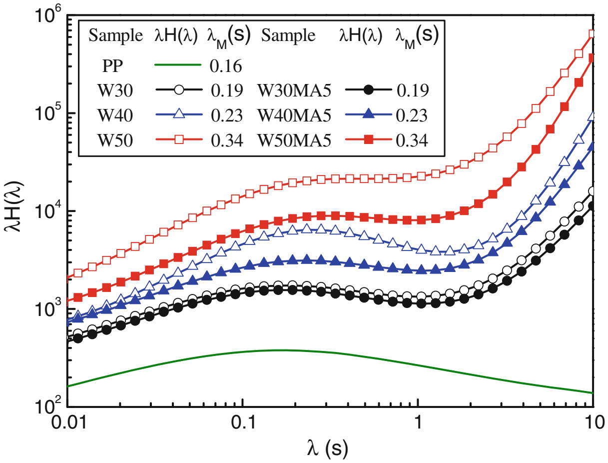


Fig. 4 Weighted relaxation spectrum for the pure PP and WPC

be ascribed to relaxation process of the wood particle agglomerates and the heterogonous interface. The effect of MAHPP is only evident when the wood content is higher. Therefore, linear viscoelasticity can clearly inflect the effect of wood particle in PP matrix from the nonterminal behavior and variation of modulus. The effect of wood content is also evident from the increasing modulus and viscosity. However, the effect of compatibilization by MAHPP cannot be differentiated when the wood content is not very high.

Nonlinear viscoelasticity

The linear viscoelasticity is really suitable to characterize the microstructure of the WPC, which can be obtained under sufficient small stress or strain amplitude. In order to determine the upper limit of the input stress σ beyond which the system is in the nonlinear region, stress sweep experiments are firstly applied at a frequency of 1 Hz in the stress amplitude range of 10 to 1000 Pa. Although, the storage modulus G' and loss modulus G'' out of linear region loses their original physical meaning and can no longer be called as storage modulus and loss modulus. The first harmonic components, G'_1 and G''_1 can be used in both linear and nonlinear region. Figure 5 shows the dependence of G'_1 and G''_1 on the stress amplitude for WPC with different contents of wood particle and the MAHPP compatibilizer. It is clear from Fig. 5 that G'_1 and G''_1 are constant at low stress level, and decrease with the stress amplitude for all composites, which is an analogous shear shinning behaviors as suggesting by Ahn et al. [39]. Both particle–polymer and particle–particle interactions may be reduced due to the microstructural anisotropy resulting from the large deformation. It makes clear that G'_1 is more sensitive to σ than G''_1 at high stress level, so only the relation between G'_1 and σ is analysed in the following paragraph. For the pure PP matrix, G'_1 remains stress-independent in the whole range of applied stress, which implies that the matrix will always show the linear

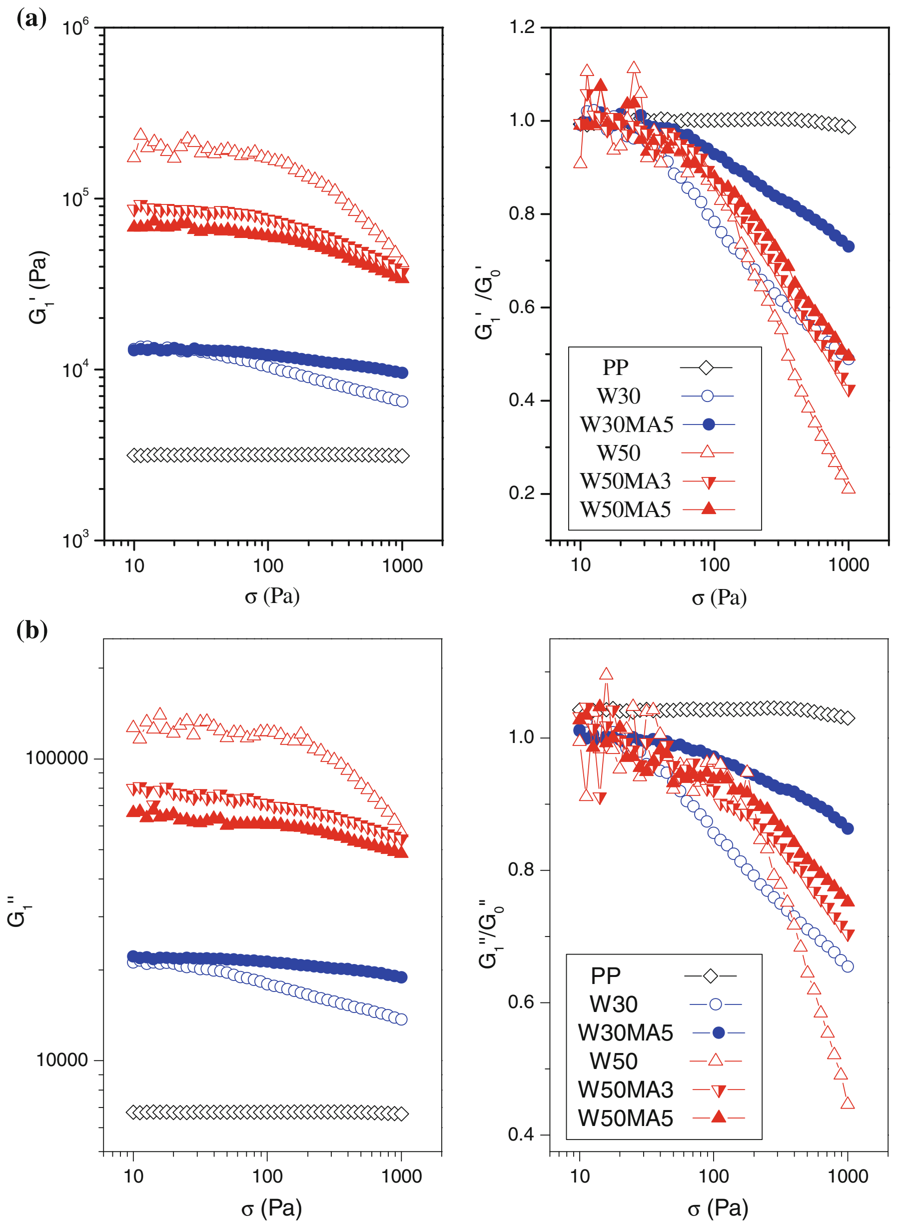


Fig. 5 Plot of G_1 vs. stress (σ) at 190 °C and 1 Hz for WPC: **a** G_1' versus σ, **b** G_1'' vs. σ

behavior and the nonlinearity in the composites can be ascribed to the structures formed by particles. The absolute value of G_1' in the linear region consistently increases with the wood content. This can be attributed to the increasing particle–particle interactions in the composites. In comparison, G_1' in the linear region of

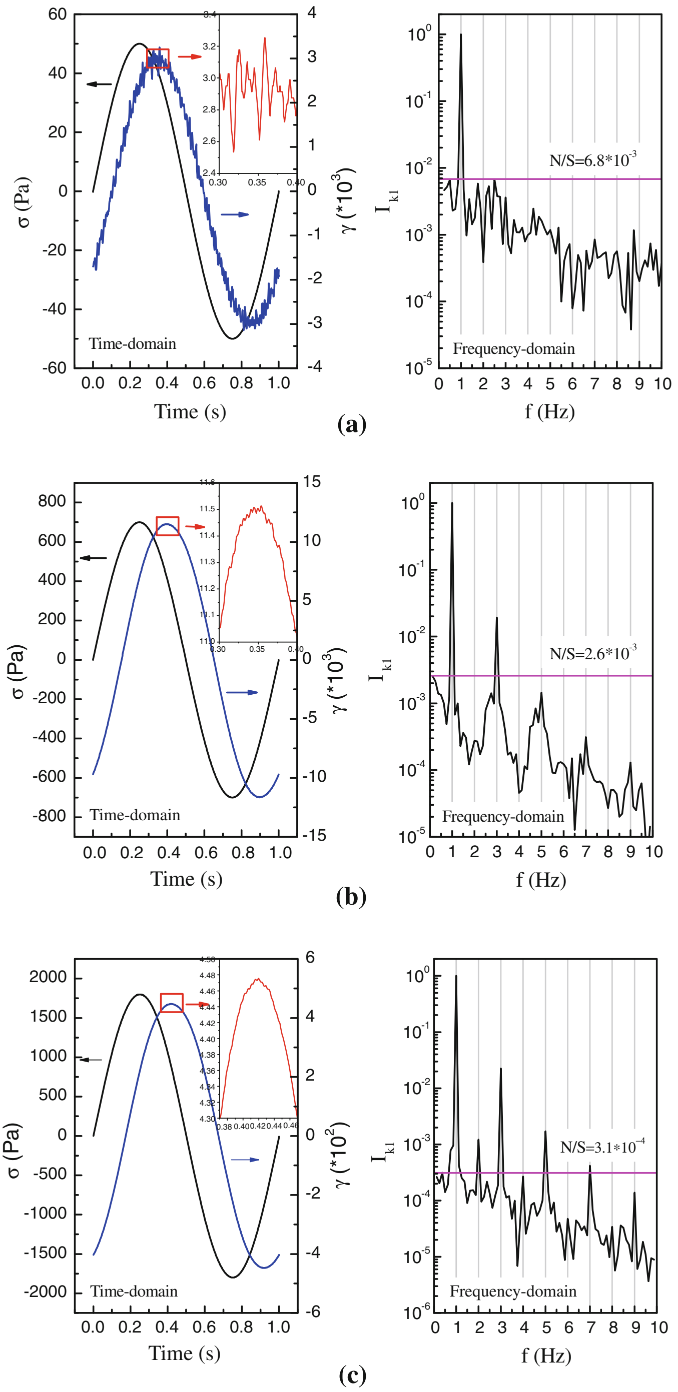
W50MA5 is lower than that of the system W50, whereas the difference in modulus is inconspicuous in the linear region for the sample with the wood content of 30 wt%, which suggests that rheological properties in linear region would be insensitive to the structure change after the addition of MAHPP. As the stress amplitude increases, the composites show nonlinear behavior and G_1' gradually decreases with the amplitude of stress. More interestingly, the decreases of G_1' with stress are more severe in the composites without MAHPP. Since the decrease of moduli with the amplitude of stress is directly related with the rupture of the microstructures in the composites, less sensitivity of modulus to the stress for composite containing MAHPP suggests MAHPP is able to stabilize the structures of wood particles.

Actually, during the stress amplitude sweep, the waveform of output signal gradually deviates from the sinusoidal form, which denotes the appearance of nonlinear behavior. This can be shown more clearly when plotting the strain signal as a function of time. Typical strain responses and corresponding power spectrum after Fourier transform for W50 at 50, 700, and 1800 Pa are depicted in Fig. 6, respectively. Although previous nonlinear oscillatory experiments on polyolefin, immiscible polymer blends, and suspensions of particles in Newtonian fluid show clearly distorted output signal [26, 29, 31], the distortion of steady strain response for W50 is not very obvious in the time domain in our experiments. However, the corresponding power spectrum after Fourier transform clearly shows that the high harmonic contributions to the strain are much more evident and the noise in output strain wave becomes gradually weaker as the applied stress increases.

As seen in Fig. 6a and b, it is clear that the strain signal is noisy and the higher harmonic contributions are so obscure with the 6.8×10^{-3} noise-to-signal ratio under the applied stress 50 Pa which suggests that the W50 sample is in the linear region. As the stress amplitude increases, the noise-to-signal ratio decreases and nonlinearity gradually appears. Higher odd harmonic contributions (I_{31}, I_{51}, and I_{71}) are present as the stress amplitude becomes larger than 700 Pa. At the same time, the occurrence of even harmonics is clearly observable in Fig. 6c. This even harmonic I_{21} can be reasonably associated to instability flow of the sample such as stick slip, or edge fracture, or asymmetric flow, which may indicate the threshold of maximum applied stress for the oscillatory experimental [3, 23, 40]. It is noticed that the approximate corresponding strain is 0.046 when the maximum applied stress at 1800 Pa as shown in Fig. 6c. Such strain is quite small and lies in the linear viscoelastic range of the PP matrix. Actually, higher harmonics cannot be observed for polypropylene under the whole range of corresponding strain. The signal intensity of 3rd harmonic is powerful enough to represent the change of microstructure in WPC when applied a large shear stress.

It has been shown that the intensity of nonlinearity increases with wood content and decreases with the amount of MAHPP. Generally, for a composite with yield stress, which might be true in this study, the rheological behavior can be simply described by Bingham model, which is expressed in oscillatory shear flow as

$$\dot{\gamma}(t) = \frac{\dot{\sigma}(t)}{G} + U\big(\sigma(t) - \sigma_y\big)\frac{\sigma(t) - \sigma_y}{\eta_0} + U\big(-\sigma(t) - \sigma_y\big)\frac{\sigma(t) + \sigma_y}{\eta_0} \qquad (7)$$


σ (Pa)
γ (*10³)
Time (s)
Time-domain
Frequency-domain
I_k1
f (Hz)
N/S=6.8*10⁻³
(a)
N/S=2.6*10⁻³
(b)
γ (*10²)
N/S=3.1*10⁻⁴
(c)

◀ **Fig. 6** The strain responses in the time domain at $f = 1$ Hz (*left picture*, peak value of stain responses magnified in *inset*) and the corresponding frequency spectra (*right picture*) after Fourier transform for W50, in which the absolute peak value of higher harmonic normalized with the that of the corresponding first harmonic. The imposed stresses are 50, 700, and 1800 Pa in (**a**), (**b**), and (**c**), respectively

where $U(x)$ is a unit step function which takes 1 when $x > 0$, and 0 when $x < 0$. The Bingham model can be phenomenologically regarded as a series of elastic springs with modulus G and a parallel combination of a dashpot (with Newtonian viscosity $\eta_0 \gtrsim$ and yield element (with yield stress σ_y) [26]. In such a case, the magnitude of I_{31} when the stress is sufficiently large only depends on $\eta_0\omega/G$, which is independent of the yield stress. The nonlinearity I_{31} is weaker for a larger $\eta_0\omega/G$. It is possible to apply this concept in WPC. Owing to the basic incompatibility between PP matrix and wood particles, the hydrophilic wood particle has a tendency to cluster together to form the particle networks, generally known as a weak solid structure and a certain amount of stress is required to break the particle networks [1, 3]. The composite will behave as a rigid body for applied stress less than σ_y. So storage modulus G' in linear region can be used as a substitute for G in the Bingham model. Once the applied stress is large enough, the weak solid structure can be broken and the composite will flow under viscous forces. Therefore, Newtonian viscosity η_0 can be approximately submitted by the complex viscosity $|\eta^*|$ at 600 Pa. The calculated results of $|\eta^*|/G'$ for different WPC system are listed in Table 2. It is clear that the value of $|\eta^*|/G'$ decreases with the wood content and increases after addition of MAHPP, which shows the same trend with I_{31}. This is consistent with the Bingham model's prediction. Moreover, the ratio $|\eta^*|/G'$ represents certain characteristic time, where the larger $|\eta^*|/G'$ suggests more stable structures inside the composites. This agrees with the dependence of G' on stress amplitude for composites with and without compatibilizers.

The parameter ϕ_{31} is the other important physical variable to characterize materials in the nonlinear region [32, 41]. For the stress sweep applied at low amplitude (in the range of 50–200 Pa), ϕ_{31} is not repeatable enough to investigate the nonlinearity. The results for ϕ_{31} only in the range of 200–1,800 Pa for WPC with different MAHPP content are present in Fig. 8, which shows the similar shape as I_{31} changes. There is a clear dependence of ϕ_{31} on the MAHPP content, and the variable range is remarkably different, i.e., fluctuating from 130° to 170° for W50 and close to a fixed value (around 155°) for W50MA5, which suggests relative

Table 2 Values of $|\eta^*|/G'$ for different WPC system in this study

Sample	G'(Pa)	$\|\eta^*\|$ (Pa·s)	$\|\eta^*\|/G'$ (s)
W30	13,589	2,544	0.19
W30MA5	13,589	3,353	0.25
W40	41,163	4,513	0.11
W40MA5	28,069	5,074	0.18
W50	197,867	10,597	0.05
W50MA3	86,640	10,185	0.12
W50MA5	68,640	11,131	0.16

phase angle alone can also be used to interpret the effect of compatibilizer. In the case with constant I_{31}, it has been shown that the maximum strain amplitude appeared at $\phi_{31} = 180°$ [21], which indicated that the composite had a poor structural stability and was more prone to deformation. This phenomenon can be interpreted as the different shear-thinning process of the sample and suggests there is the effect of MAHPP on the structural stabilization, which is in agreement with the nonlinear intensity as reflected by I_{31}. Furthermore, this result implies that ϕ_{31} is appropriate for distinguishing the structure in nonlinear region.

In order to further elucidate the nonlinear behaviors, strain–stress Lissajous figures are also presented in the inset of Fig. 8. In the linear region, the Lissajous curves appear as an ellipse, which will be more like a straight for the strongly elastic materials and become fattened for the viscous materials. The shape of Lissajous curves will be distorted from the normal ellipse to be more complicated, when materials is in the nonlinear region [21]. As shown in Fig. 8, the change of phase angle as the stress amplitude increases from 500 to 1,500 Pa is evident. This phenomenon is consistent with relative phase angle. Comparing the Lissajous curves in both Figs. 7 and 8, we can confirm that the nonlinear intensity I_{31} and phase shift angle ϕ_{31} are really dependent on the type of the structure variation for composites with the same wood particle content.

Figure 9 shows the dependence of relative phase angle on the stress amplitude. For the system without MAPP, it is clear that ϕ_{31} will increase with the stress amplitude at low stress level, reach a maximum and then decrease slightly with the stress amplitude. At the same time, the value of ϕ_{31} is small under small stress amplitude and is large under large stress amplitude. This implies that the response of the actual strain amplitude increases with the stress amplitude, that is, moduli reduction is more pronounced under large stress amplitude. However, in comparison with the same wood content system, ϕ_{31} for composite containing MAHPP shows a

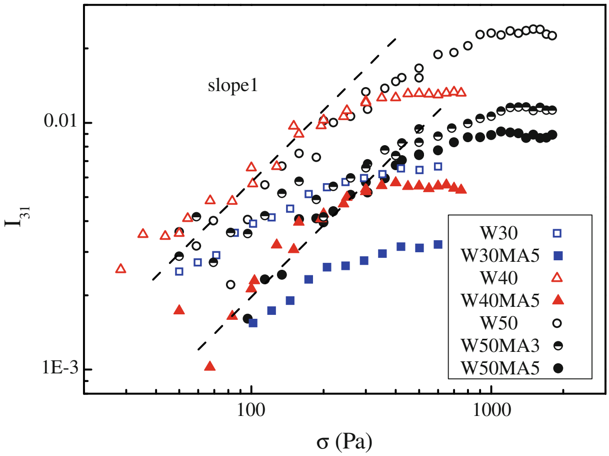


Fig. 7 The steady intensity value of the third harmonic normalized by that of the corresponding first harmonic (I_{31}) as the function of the imposed stress amplitude for the WPC filled with different contents of wood particle and MAHPP compatibilizer

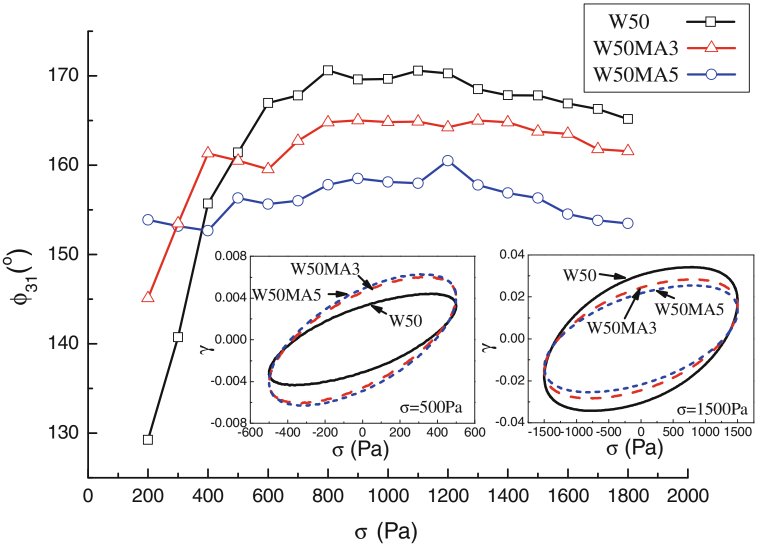


Fig. 8 Phase shift angle ϕ_{31} as the function of the stress amplitude. ϕ_{31} is defined according to Eq. 6

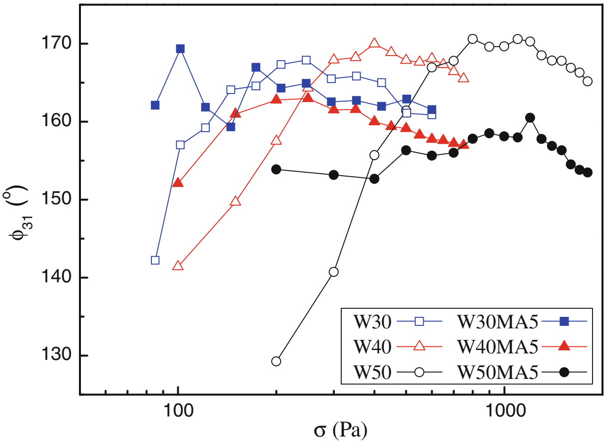


Fig. 9 Relative phase angle ϕ_{31} as a function of stress amplitude for WPC

quite different tendency that it exhibits a relatively larger value at initial stress amplitude and the rise of ϕ_{31} at large stress level is not evident. This is related to the change of structures during oscillatory shear, which suggests the nonlinear behavior has less effect on the actual stain amplitude and MAHPP makes an obvious contribution to the structure stabilization of WPC system. In addition, the discrimination of ϕ_{31} at higher stress level is more evident with the increase of the filled fraction. This phenomenon illustrates that the compatibilization effect of MAHPP at the interface between wood particle and PP matrix has brought noticeable achievements especially for the high wood particle filled system.

Moreover, there is a clear distinct nonlinear behavior between the sample W30 and W30MA5, although the frequency sweep result for both of them are same in the linear region (as shown in Fig. 2). Adding a small amount of MAHPP compatibilizer can dramatically change microstructure such as decreasing the nonlinear intensity and diminishing variation range of ϕ_{31} for sample W30MA5. It implies that long relaxation structure can be easily distinguished in the nonlinear region.

The FTR result indicates the nonlinear properties of WPC in our experimental depend on both the quantity of wood particle and the type of interfacial hydrodynamic interaction. Therefore, it is needed to understand the nature of interfacial hydrodynamic interaction in the WPC system. The particle–particle interactions as well as particle–polymer matrix interactions increase with the content of the wood particle (as show in Fig. 2). According to the calculated relaxation spectra, the structure of wood particle aggregates and the interface exhibit the longer relaxation behavior (as shown in Fig. 3), suggesting those large-scale structures seem to be easily destroyed in the same timescale compared with the chains of PP matrix. Referring to the previous study results [33, 42–44], a possible origin of the nonlinear phenomena in filled system is that the applied stress can induce the irreversible change of structure due to the particle orientation or particle migration. Considering the small amplitude of the strain response and high viscosity of the matrix in this experimental, the microstructural changes of WPC may mainly be attributed to the irregular wood particles orientation to the flow direction [1]. When the applied stress exceeds the critical stress, it provides the adequate energy for the irregular particles to deviate from the equilibrium position. Once the particles yield irreversible orientation, the particle agglomerates fail to reform and gradually collapse until forming randomly dispersed particles, therefore, the WPC system exhibits the nonlinear properties. In addition to the gradually collapse of the networks, the particle–polymer matrix interaction is the other origin of the nonlinear phenomenon. Actually, the interfacial PP layers around the wood particles experience a much higher local shear deformation than the apparent strain amplitude and there is complicated disturbance near the interface during the orientation of the anisotropic solid particles, which may lead the PP molecules nearly the interface are inclined to disentangle in macroscopic space-scale [42, 44, 45]. Therefore, the rheology of noncolloidal suspensions is highly sensitive to the particle orientation. This is why the nonlinear properties of the WPC are easily be detected in quite small macroscopic strain amplitude at 1 Hz (as shown in Fig. 6b, c).

The MAHPP compatibilizer is generally bifunctional molecules with the side chains capable of adhering to the wood particles and the main chains entangled with the polymer [9]. With small amount of MAHPP can basically alter the character of the interface, thus it helps the PP matrix to wet the particle better (as shown in Fig. 3). At the same time, the relative low molecular weight MAHPP has the effect of internal lubricant on the inter-particle interaction and it can change the agglomerated particles from the half dry friction to half fluid friction, thereby reducing the modulus in the linear region especially for the high-filled system (as show in Fig. 2) [1, 3, 19]. In other words, both of wood particle–polymer interfacial characters and particle–particle interaction properties in the WPC system have been changed after adding the MAHPP compatibilizer. Hence the orientational wood particles do get more opportunity to recover to the equilibrium position and compatibilizer can really stabilize the system in the nonlinear region (as shown in Figs. 7, 8, and 9).

Therefore, depending on the system whether containing MAHPP compatilizer or not, there is the same type of hydrodynamic interaction among those systems with different wood content. The particle–particle interaction and particle–polymer interfacial contribution are increased as the wood content rises, thus it leads that the I_{31} intensity of WPC with different wood content is nearly overlapping in relative lower applied stress and the value of critical stress and I_{31} intensity after the turning point ascend with the wood particle content.

Conclusions

The rheological properties of WPC samples with respect to wood particle loading and MAHPP compatibilizing effect have been studied from linear region to nonlinear region in this article. Owing to the particle–particle interactions and particle–polymer interaction gradually strengthen with the filler loading, the WPC system exhibits the higher moduli compared with those of the pure PP. The adding of MAHPP in WPC system leads to obviously compatibilizing effect between the heterogonous interphase, which confirmed by the SEM results. The role of MAHPP can be evident in linear viscoelasticity when the wood content is sufficiently high. However, it is hard to elucidate the effect of compatibilizer for composites with low wood content in linear viscoelastic region. Rheological properties at nonlinear region are found to be very sensitive to the small amount of compatibilizer. The nonlinear properties such as nonlinear intensity I_{31} and phase shift angle ϕ_{31} obtained from FTR have been proved to be related to the structures of wood particles. As the MAHPP content increases, the WPC system displays significant decrease in the value of I_{31} and the variation range of ϕ_{31} in nonlinear region. Since the gradual collapse of the local wood particle agglomerates and the disentanglement of PP interfacial layers near the orientation wood particles are the origin of the nonlinear properties in WPC system, the decreased value of I_{31} and ϕ_{31} are believed to be related to the stability of structures when MAHPP is added. Therefore, the nonlinear behaviors have been proved to be a sensitive parameter to characterize the effect of compatibilizer in wood–polymer composites. Such method is believed to be effective to evaluate the compatibilizing effect in other polymer composites.

Acknowledgments This study is partly supported by Shanghai Leading Academic Discipline Project (No. B202). W. Y. is supported by the SMC project of Shanghai Jiao Tong University.

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