STRESS RELAXATION OF WOOD FLOUR/POLYPROPYLENE COMPOSITES AT ROOM TEMPERATURE

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Abstract. To investigate the time-dependent property of wood flour/polypropylene (PP) composites and the effect of coupling agents on it, both tensile stress relaxation and compressive stress relaxation curves were determined at various wood contents (0, 20, 30, 40, 50, 60, and 70%) without a coupling agent and were also determined at 50 and 60% wood contents with different coupling agents such as maleic anhydride grafted polypropylene (MAPP) and silane. Bending modulus of rupture (MOR) and modulus of elasticity (MOE) of wood flour/PP composites at various wood contents without coupling agents and at 60% wood content with MAPP and silane as coupling agents were also tested to compare with stress relaxation results. All measurements were performed at 26 ± 1°C. Results showed that 1) the tensile stress relaxation appeared to have similar trends with compressive stress relaxation (They both declined obviously after adding coupling agents at the same wood content.); 2) wood content had a great influence on stress relaxation behavior of wood flour/PP composites (The lowest stress relaxation rates appeared at 40% wood content for both tensile and compressive stress relaxation of wood flour/PP composites without coupling agent, suggesting the best compatibility between wood and PP is at about 40% within the experimental conditions of this study.); 3) optimal loading level of a coupling agent for stress relaxation varied with type of coupling agents and wood content (Within the experimental conditions used in this study, the optimal loading level for MAPP was 2% at both wood contents, whereas for silane, it was 1.5% at 50% wood content and 2% at 60% wood content.); and 4) lower stress relaxation rates corresponded to higher bending MOR and MOE values at 60% wood content. This suggests that long-term performance of wood flour/PP composites would be consistent with bending strength at room temperature.

Keywords: Wood flour/polypropylene composite, wood flour content, coupling agent, stress relaxation.

INTRODUCTION

Recently, wood flour/polymer composites have been widely applied in fields such as construction, mobile homes, packaging, transportation, and furniture because of their relatively low cost and good performance. However, incompatibility between wood and polymers caused by their great interfacial energy gap is always a problem in further improving properties of wood flour/polymer composites. In addition, high wood contents usually correspond to poor dispersion of wood flour in composites because of hydrogen bonding among hydroxyl groups of wood, which poses difficulty in making composites more efficient. Adding coupling agents such as silane, titanate, aluminate, isocyanate,

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and polar monomer grafted polyolefin is one of the ways to improve composite properties by improving interfacial compatibility (Raj and Kokta 1991; Schneider 1994; Oksman and Lindberg 1995; Oksman 1996). However, previous investigations mostly focused on physical and mechanical properties and seldom discussed time-dependent properties such as stress relaxation and creep.

Stress relaxation refers to the fact that at a fixed strain, stress resistance to deformation decreases with increasing time (Cao et al 2006). When a material is elongated, compressed, or undergoes other deformations within the elastic region, a stress would produce in the material to try to bring the material back to its original form. If the deformation is fixed, then the stress will decrease with the breaking of original bonding and the formation of new bonding. When the stress is completely relaxed, a permanent deformation takes place. Therefore, stress relaxation can serve as an indicator of long-term dimensional stability. A faster stress relaxation suggests an inferior dimensional stability in the long term. In previous studies, the stress relaxation approach has been used to investigate time-dependent properties of modified wood and the interaction between wood and wood-modifying chemicals such as formaldehyde-treated wood (Inoue et al 1994; Nakano 1996), preservative-treated wood (Cao et al 2006), heat-treated wood (Dwianto et al 1997, 1998), and other kinds of modified wood (Xue and Zhao 2006; Fu and Zhao 2008). Bhattacharyya et al (2006) investigated stress relaxation under constant strain of wood fiber/thermoplastic composites produced by either injection molding or hot pressing at 25, 50, and 80°C and found that adding wood fibers as reinforcement in the composite restricted stress relaxation, but effectiveness decreased with increasing temperature. They also found that composites made by hot pressing exhibited lower stress relaxation than those made by injection molding. Dastoorian et al (2010) investigated creep and stress relaxation of wood flour/high-density polyethylene composites at 67% wood content. They compared stress relaxation by using four ultimate strain levels including 30, 40, 50, and 60% of original dimension and concluded that the studied wood flour/polyethylene composite was a kind of rheologically simple material. In our previous study, we did a pilot study on viscoelastic properties of maleic anhydride grafted polypropylene (MAPP)-modified wood flour/polypropylene (PP) composites (WPC) by both compression stress relaxation method and dynamic mechanical analyses. Results suggested that a suitable loading level of MAPP had a positive effect on viscoelastic properties of WPC at high wood to polymer ratios, and excessive MAPP loading would have resulted in adverse effects (Cao et al 2010).

However, until now, stress relaxation of wood flour/polymer composites at different wood contents as well as the effect of coupling agents on them has not been well understood. Therefore, the objective of this study was to investigate both tensile and compressive stress relaxation curves of WPC with various wood contents as well as the effect of coupling agent on stress relaxation behavior. Results should provide useful information on evaluation of long-term performance of wood flour/polymer composites and the determination of coupling agent loading levels.

MATERIALS AND METHODS

Materials

Poplar (*Populus tomentasa* Carr) wood flour of 100 mesh size and PP with density of 0.9 g/cm^3 were used as raw materials to prepare WPC. PP has a melting point of about 165°C and a melt flow index of 1.5 g/10 min. The coupling agents used in this study included MAPP and silane (γ-methacryloxypropyltrimethoxysilane, $CH_2 = C [CH_3] COOCH_2CH_2 CH_2Si [OCH_3]_3$) with density of 1.04 g/cm^3, which is designated as KH-570 (Chinese Academy of Science). Polyfluorotetraethylene membranes were used as demolding materials to prevent the board from sticking during hot pressing.

Wood Flour/Polypropylene Composite Manufacturing

WPC with target density of 1 g/cm^3 were 270 × 270 × 3 mm (thickness). Selected wood contents for WPC without a coupling agent were 70, 60, 50, 40, 30, 20, and 0%. For 50 and 60% wood contents, six different MAPP loading levels (0.5, 1, 1.5, 2, 4, and 8% of wood flour and PP total weight) and silane loading levels (0.5, 1, 1.5, 2, 3, and 5% of wood flour and PP total weight) were used.

Wood flour, PP, and coupling agents were weighed and then blended in a high-speed mixer. The mixture was then dried in an oven at 105 ± 1°C for 2 h and taken out for hand matting. A hot press (SYSMEN-II, made by Chinese Academy of Forestry) was used to compress the mat at 180°C and 4 MPa for 6 min. After hot pressing, the formed mat was pressed at 4 MPa for another 6 min at room temperature in a cold press. The same method was used to prepare mats of PP controls.

Stress Relaxation Determination

Tensile and compressive stress relaxation tests were performed on the self-assembled equipment at 26 ± 1°C. See Cao et al (2006) for the equipment diagram. The test for each sample in air-dried condition lasted 3000 s. Samples were 100 × 10 × 3 mm (thickness) for tensile stress relaxation and 10 × 10 × 3 mm (thickness) for compressive stress relaxation. Tensile strain was 1 mm (1% of its original length), and compressive stain was 20% of its original thickness. Three replicates were used for each condition.

Mechanical Property Determination

Three-point flexural tests were carried out at room temperature according to procedures described in Chinese standard GB/T9341-2000 (State Bureau of Quality and Technical Supervision 2000). 60 × 25 × 3 mm (thickness) samples were conditioned in the humidity chamber at 26 ± 1°C and RH 65 ± 5% prior to tests. In the tests, descending speed was 1 mm/min. Average bending modulus of elasticity (MOE) and modulus of rupture (MOR) of five replicates were taken as final results.

RESULTS AND DISCUSSION

Stress Relaxation of Wood Flour/ Polypropylene Composites

Tensile/compressive stress relaxation curves of composites were expressed as the change in ratio of instantaneous stress σ (t) to initial stress σ (0) with ongoing time. Tensile and compressive stress relaxation curves of WPC with or without coupling agents were all tested in this study.

Stress Relaxation of Wood Flour/ Polypropylene Composites Without Coupling Agent

Tensile and compressive stress relaxation curves without coupling agent are shown in Figs 1a and b, respectively. For the PP control panel at 0% wood content, the most significant stress relaxation was observed. It is suggested that PP control was inclined to deformation after long-term loading. After adding different contents of wood flour, the stress relaxed slower, revealing that long-time deformation can be decreased by combining two materials. Both tensile and compressive stress relaxation curves showed similar effects of wood content, namely, the stress relaxation became slower with increasing wood content and then faster again after reaching the slowest at 40% wood content.

To make it more clear, rate of stress relaxation was defined as the slope of a double logarithm curve of σ (t)/σ (0) vs time. As shown in Fig 1, stress decreased with time in an exponential trend, which corresponded to a linear relationship when plotted in a double logarithm form. Cao et al (2006) gives the detailed procedure. Before a relaxation time of 1000 s, the linear relationship was very clear and showed little sign of deviation. Therefore, the slope of the double logarithm curve of σ (t)/σ (0) vs t (t < 1000 s) was finally taken as the rate of stress

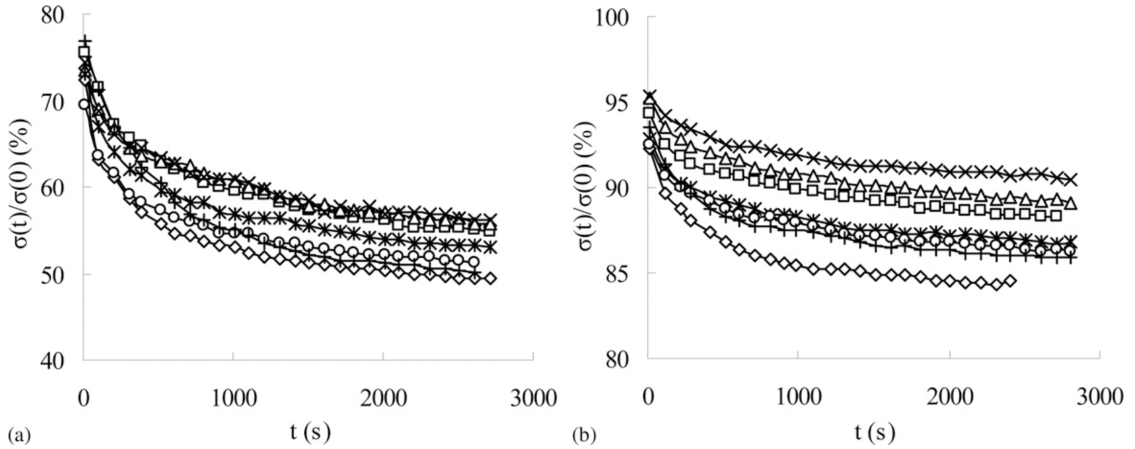

Figure 1. Tensile and compressive stress relaxation curves of wood flour/polypropylene composites without coupling agent at room temperature (a: tensile stress relaxation curves; b: compressive stress relaxation curves). Wood content: ◇: 0%, □: 20%, Δ: 30%, ×: 40%, *: 50%, O: 60%, +: 70%.

Table 1. Tensile stress relaxation rate (γ_t) and compressive stress relaxation rate (γ_c) of wood flour/polypropylene composites at various wood contents without coupling agent.

Wood content (%)	$\gamma_t \times 10^2$	R^2	$\gamma_c \times 10^2$	R^2
0	8.71	0.99	2.37	0.97
20	7.36	0.95	1.53	0.91
30	6.05	0.94	1.50	0.95
40	5.74	0.96	1.20	0.92
50	7.24	0.98	1.60	0.97
60	7.41	0.98	1.63	0.91
70	8.33	0.96	1.93	0.89

relaxation. Rates of stress relaxation are listed in Table 1 as well as values of R^2, which ranged from 0.96 to 0.99 for tensile stress relaxation and from 0.89 to 0.97 for compressive stress relaxation, suggesting good linearity between the double logarithm of stress and time during this period.

Rates of stress relaxation at 40% wood content decreased from 0.0871 to 0.0574 for the tensile approach and from 0.0237 to 0.0120 for the compressive approach. However, with wood content increasing to 70%, rates of stress relaxation began to approach the values of PP control, which had no added wood flour. It was also found that rates of stress relaxation obtained by both tensile and compressive approaches differed greatly. Rate of stress relaxation obtained by the compressive approach was much lower than that by the tensile approach. Therefore, the value of stress relaxation rate is greatly dependent on the method used and also the parameters adapted. Values obtained from different approaches of stress relaxation cannot be compared.

Stress Relaxation of Maleic Anhydride Grafted Polypropylene-Modified Wood Flour/Polypropylene Composites

Figure 2 shows the tensile and compressive stress relaxation curves of WPC at different MAPP loadings and two wood contents, 50 and 60%. Although 40% wood content appeared the lowest in stress relaxation as previously discussed, higher wood contents are always the objective in real applications. By using coupling agents, wood contents can usually be increased to some extent.

As shown in Fig 2 and Table 2, the trend of tensile stress relaxation of MAPP-modified WPC was similar to that of compressive stress relaxation. At both wood contents, composites without MAPP added (0%) showed greater stress relaxation than did MAPP-modified composites,

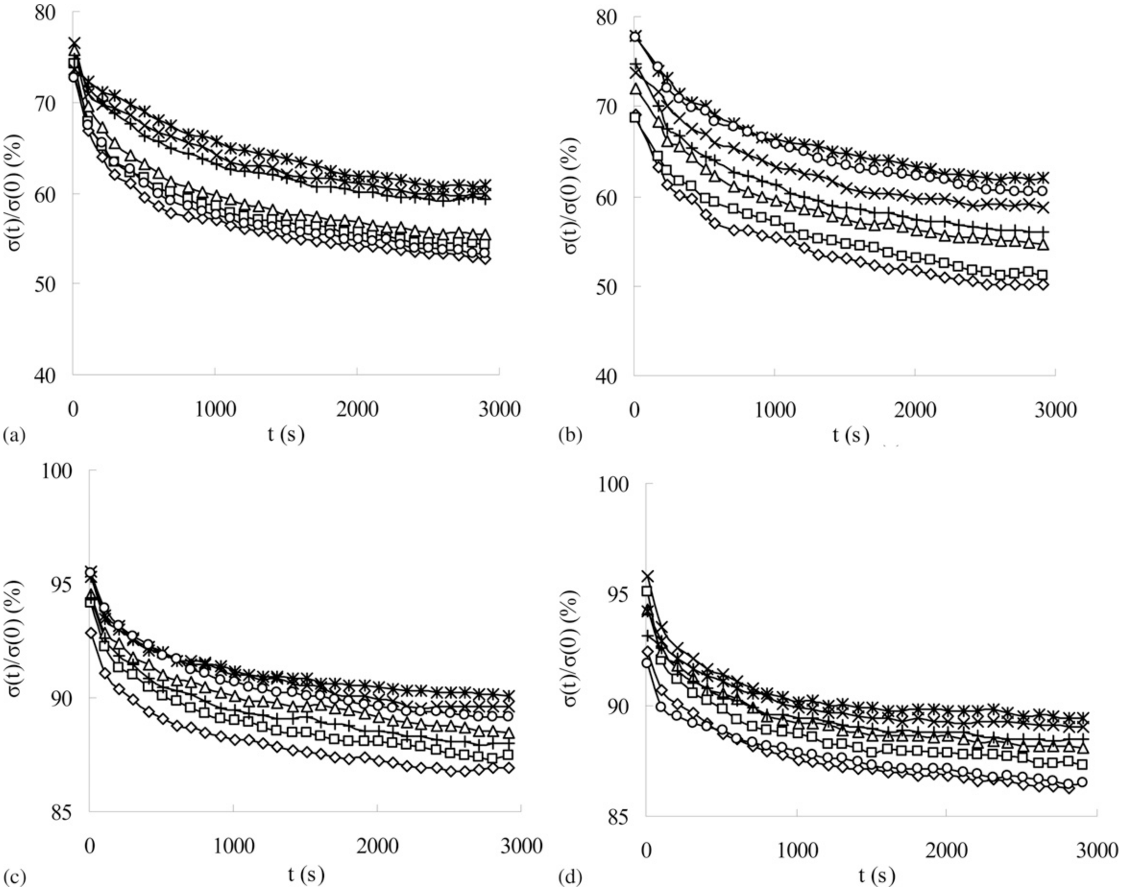

Figure 2. Tensile (a, b) and compressive (c, d) stress relaxation curves of wood flour/polypropylene composites modified with maleic anhydride grafted polypropylene (MAPP) at room temperature (a–c: wood content 50%; b–d: wood content 60%). MAPP loadings: ◇: 0%, □: 0.5%, Δ: 1%, ×: 1.5%, *: 2%, O: 4%, +: 8%.

Table 2. Tensile stress relaxation rates (γ_t) and compressive stress relaxation rates (γ_c) of wood flour/polypropylene composites with MAPP as a coupling agent.

Wood content (%)	MAPP loading (%)	$\gamma_t \times 10^2$	R^2	$\gamma_c \times 10^2$	R^2
50	0.5	7.29	0.98	1.83	0.96
	1	6.98	0.98	1.49	0.89
	1.5	5.17	0.94	1.50	0.92
	2	4.32	0.84	1.43	0.95
	4	6.98	0.96	1.45	0.93
	8	4.95	0.93	1.49	0.93
60	0.5	6.91	0.89	1.60	0.98
	1	6.38	0.91	1.49	0.93
	1.5	4.97	0.87	1.38	0.98
	2	4.75	0.90	1.35	0.92
	4	4.97	0.89	1.42	0.97
	8	6.25	0.94	1.47	0.99

MAPP, maleic anhydride grafted polypropylene.

indicating that addition of MAPP to WPC is a positive factor to inhibit long-term deformation. However, the slowest stress relaxation did not appear at the highest MAPP loading of 8% but was observed at MAPP loading 2% for both wood contents and both tensile and compressive approaches. The fact that MAPP reacts with hydroxyl groups in wood flour to form chemical bonds and tangles with molecular chains of PP results in strong internal bonding and small relative displacement, which explains the decreased stress relaxation of WPC with MAPP loading increases (Filex and Gatenholm 1991; Kazayawoku et al 1997). However, excessive MAPP molecules may have had a negative effect on compatibility between wood flour and PP, which resulted in the faster stress relaxation when MAPP loading exceeded 2%.

Stress Relaxation of Silane-Modified Wood Flour/Polypropylene Composites

Figure 3 shows tensile and compressive stress relaxation curves of silane-modified WPC at 50 and 60% wood contents. Rates of stress relaxation are listed in Table 3. As shown in Fig 3 and Table 3, trends for stress relaxation of silane-modified WPC were similar to those of MAPP-modified WPC except that the slowest stress

Table 3. Tensile stress relaxation rate (γ_t) and compressive stress relaxation rate (γ_c) of wood flour/polypropylene composites with silane as coupling agent.

Wood content (%)	Silane loading (%)	$\gamma_t \times 10^2$	R^2	$\gamma_c \times 10^2$	R^2
50	0.5	6.93	0.93	1.53	0.92
	1	5.87	0.91	1.35	0.99
	1.5	5.77	0.98	1.31	0.98
	2	5.85	0.95	1.32	0.95
	3	6.89	0.97	1.57	0.98
	5	6.13	0.93	1.53	0.99
60	0.5	7.39	0.97	1.66	0.94
	1	6.76	0.97	1.69	0.93
	1.5	6.91	0.95	1.41	0.96
	2	3.56	0.85	1.11	0.98
	3	4.68	0.88	1.14	0.97
	5	5.82	0.92	1.67	0.98

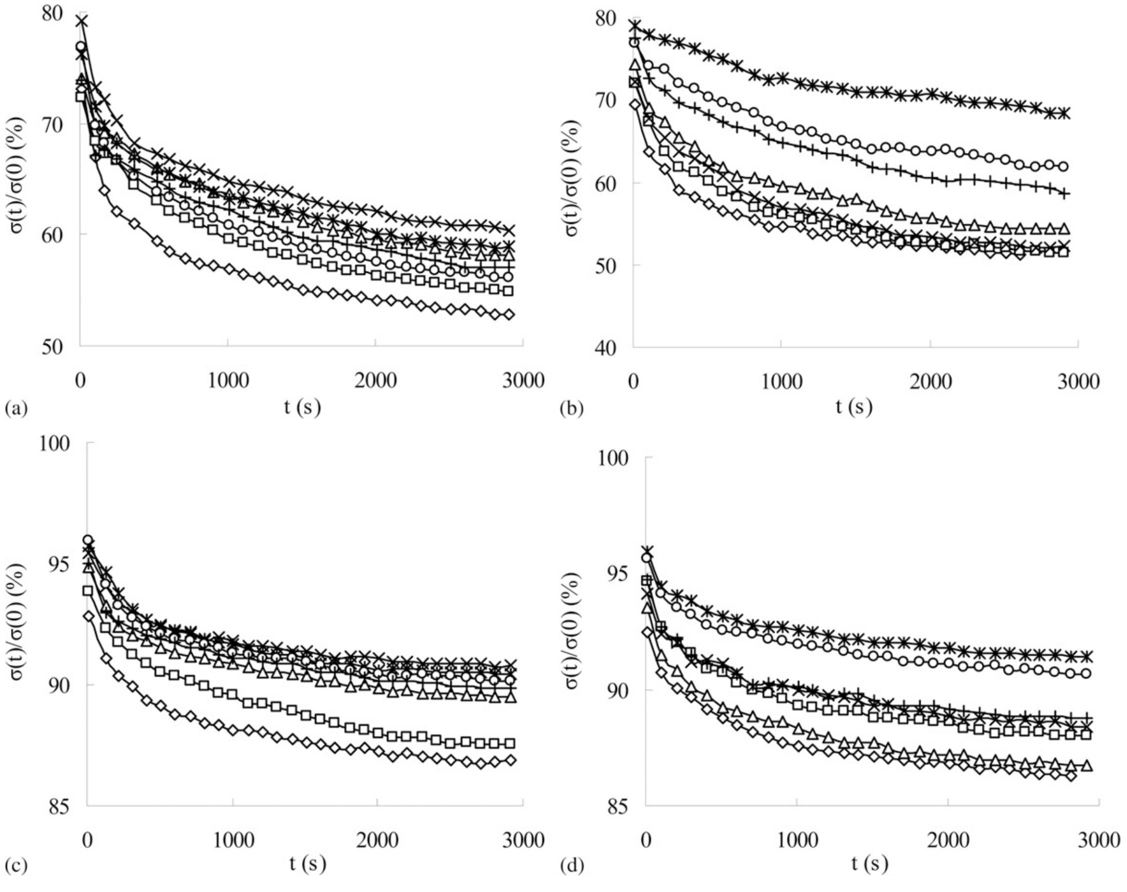

Figure 3. Tensile (a, b) and compressive (c, d) stress relaxation curves of wood flour/polypropylene composites modified with silane coupling agent at room temperature (a–c: wood content is 50%; b–d: wood content is 60%). Silane loadings: ◇: 0%, □: 0.5%, Δ: 1%, ×: 1.5%, *: 2%, O: 3%, +: 5%.

relaxation was observed at a silane loading of 1.5% at 50% wood content. However, at 60% wood content, the slowest stress relaxation still appeared at 2% silane loading, which is the same as MAPP. It is suggested that for a silane coupling agent, 1.5% might be enough to improve composite properties at 50% wood content. Silanol is generated by hydrolysis of alkoxyl in organosilane. It can react with hydroxyl groups in wood flour to decrease the polarity of wood flour, and the long chains of organosilane and PP can be twisted with each other forming strong interfacial reaction and improves bonding strength effectively (Matuana et al 1999). However, as is the case with MAPP, excessive silane molecules may also have a negative effect on compatibility between wood flour and PP, decreasing the properties.

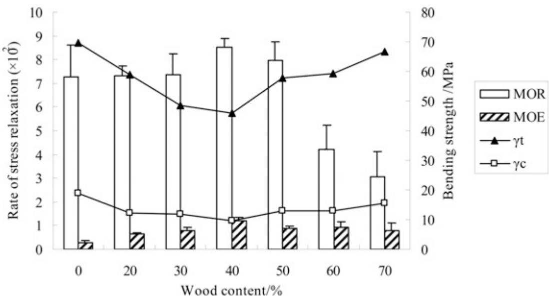

Figure 4. Relationship between bending modulus of elasticity (MOE), modulus of rupture (MOR), and rates of tensile and compression stress relaxation of wood flour/polypropylene composites without coupling agent.

Mechanical Properties of Wood Flour/ Polypropylene Composites

As shown in Fig 4, MOR and MOE of WPC without a coupling agent both increased first and decreased thereafter with increasing wood content and the highest values appeared at 40% wood content, which exactly corresponds to the lowest rate of stress relaxation. It appears that the trend of MOE fits much better than that of MOR with the change of stress relaxation rates. This is reasonable because stress relaxation is defined as the stress change at a small fixed strain, which should be located in the elastic region in the stress–strain curve.

Bending MOR and MOE of WPC modified with both coupling agents at 60% wood content were plotted in Fig 5 together with tensile and compressive stress relaxation rates. After adding a coupling agent, the relationship between

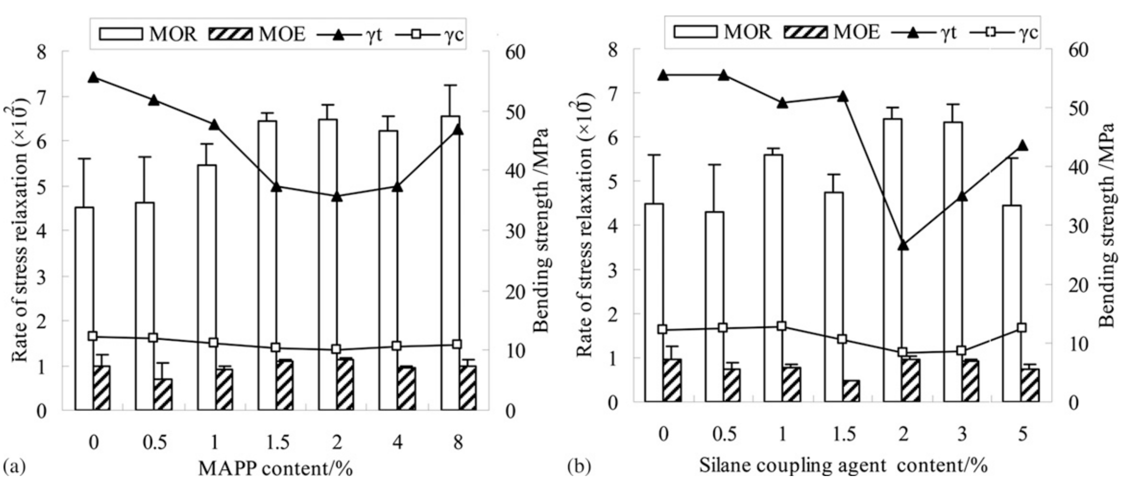

Figure 5. Bending modulus of elasticity (MOE), modulus of rupture (MOR), and rates of tensile and compression stress relaxation of wood flour/polypropylene composites modified with maleic anhydride grafted polypropylene (MAPP) and silane at 60% wood content (a: MAPP; b: silane).

mechanical properties and stress relaxation appeared somewhat complicated. For MAPP-modified composites, MOR clearly increased with increasing MAPP loading below 1.5% and thereafter changed little. MOE appeared to decrease at first after adding MAPP, then increased with MAPP content below 1.5 or 2%, and then decrease again. However still, MAPP content of 1.5 or 2% is a suitable loading level to obtain optimal mechanical properties as well as long-term performance. For silane-modified composites, high MOR and MOE values were obtained at 2% and 3% silane loading, whereas the slowest stress relaxation was also observed at 2%. However, after 3%, MOR and MOE both decreased. This suggests that both mechanical and stress relaxation properties were very sensitive to silane loading compared with MAPP loading. Therefore, the selection of silane loading is very critical.

CONCLUSIONS

By using two stress relaxation approaches to study long-term performance of WPC without coupling agents and with MAPP or silane as coupling agents, we can draw the conclusions that both approaches are very consistent in showing the trends and therefore adaptable in studying long-term performance of wood/polymer composites. For WPC without a coupling agent, 40% wood content was the best for both mechanical properties and long-term performance within the experimental conditions in this study. At higher wood content such as 60%, mechanical properties and long-term performance can be improved by adding suitable amounts of coupling agents. The optimal amount varies with many parameters including wood content and type of coupling agent. In this study, we found that at 60% wood content, mechanical properties and long-term performance can both reach high values at a MAPP loading of 1.5 or 2.0% or a silane loading of 2.0%.

Stress relaxation showed very good consistency with mechanical properties at room temperature as shown in this study. In our future research, the effect of temperature on stress relaxation of WPC with or without coupling agents will be further investigated and also the mechanism will be discussed in detail.

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