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Composites of wood and *trans*-1,4-isoprene rubber I: Mechanical, physical, and flow behavior

Abstract The modification of *trans*-1,4-isoprene rubber (TIR) with maleic anhydride (MAH) was conducted in a kneader at 150°C, 30–70 rpm, for 10 min without using peroxide. The resultant MAH-modified TIR (MTIR) was then evaluated as a compatibilizer for TIR–wood flour (WF) composites. A control composite composed of TIR and WF only was also prepared. The presence of WF in the TIR–WF composite worsened the tensile and some physical properties. The addition of 5% MTIR as a compatibilizer to the whole composite improved the mechanical and the physical properties and increased the flow temperature and the melt viscosity. The improved composite had a 2.5 times increase in tensile strength and absorbed considerably less water than did the control composite. The SEM micrograph proved that interaction and adhesion between TIR and WF could be improved by the MTIR compatibilizer. The composites of TIR–MTIR–WF melts were of pseudoplastic nature, and their flows obeyed the Ostwald de Waele power law equation.

Key words *Trans*-1,4-isoprene rubber (TIR) · Maleic anhydride-modified TIR · Wood flour · Compatibilizer · Composite

Introduction

Because of their good processibility and ability to be recycled, the moldable wood–plastic composites from wood

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meals and synthetic polymers are enjoying a rapid growth in use and have been intensively studied by several researchers.[1-7] Filler is added to the polymer matrix with the aim of improving thermal and mechanical properties. Forestry activities, such as the harvesting and wood industries, produce huge amounts of waste. These wastes are usually utilized as relatively valueless products such as fuels for boilers or are burned without meaningful utilization and become a problem for the environment. An efficient use of natural resources is proposed as a desirable way to minimize the negative impact on the environment on one hand and to minimize the exploitation of resources on the other hand. Several other lignocellulosic materials, such as bagasse, nut shells, corncobs, bamboo, and cereal straws, have also been tried.

Composites based on natural wood/cellulose fibers as a reinforcing filler offer a number of benefits: high specific stiffness and strength, desirable fiber aspect ratio, usability, flexibility during processing with no mechanical harm to the equipment, low density, biodegradability, abundance as raw materials, and finally low cost per unit volume. The reinforcing filler plays an important role in strengthening the composite by effective transfer of stress between the fiber and the matrix. Despite the advantages mentioned above, the use of cellulose fibers combined with thermoplastics in general has not been extensive. Possible reasons, all of which contribute to unsatisfactory final properties of the composite, include limited thermal stability during processing, poor dispersion characteristics of the filler in the thermoplastic melt, and its limited compatibility with the matrix. In this connection, coupling or compatibilizing agents have been tested to improve dispersion, adhesion, and compatibility for the system. These agents can modify the interface by interacting with both the fiber and the matrix, thus forming a link between the components. It has been reported in the of literature[1-4,7,8] that maleic anhydride (MAH) can be introduced into polymers, such as polypropylene, polyethylene, and acrylonitrile-butadiene-styrene copolymer (ABS), through a radical coupling addition to form MAH-modified polymer in the presence of peroxide. The MAH-modified polymer can then further react with the

polymer having an -OH or NH_2 end-group to form a long-chain graft copolymer that can be used as a compatibilizer of the incompatible polymer blends. MAH introduced in this way into synthetic polymers has been proved to form ester linkages when reacting with hydroxy groups on the wood flour (WF) interface.

One environmentally friendly material is *trans*-1,4-isoprene rubber (TIR). TIR is an elastomer and in nature is biodegradable; it is known as balata or gutta percha. This polymer has a high level of crystallinity, which leads to good strength properties at normal temperature and at a temperature near or above the crystalline melting point; the polymer is easy to process.[9] Furthermore, TIR is vulcanizable owing to the presence of an unsaturated bond (C=C). The raw polymer or the raw polymer compounded with conventional compounding ingredients may be used without vulcanizing agents in a wide variety of applications where the strength at ambient temperature is important. Such applications include medical casts, adhesives, and moldable sheets.

With these facts before us, in the present study we tried to develop biodegradable moldable wood–TIR composites to obtain a compatible blend with excellent physical, mechanical, interfacial, and flow properties.

Experimental

Materials

TIR was supplied by the JSR Co., and MAH was purchased from Nacalai Tesque Inc. and was used as received. The filler used was WF that passed through a 200-mesh sieve.

Preparation of MAH-modified TIR

TIR and 10% or 20% MAH were reactively blended in the melt state in the kneader (Toyo seiki labo-plastomill LPM 18–125) at 110°–160°C and 30–70 rpm for 10 min. Kneading TIR in the presence of MAH at such a high temperature (110°–160°C) might cause crosslinking during the treatment, but it was found that even the maleroyrated TIR prepared at 160°C revealed flow behavior as high as 102°C when using the flow tester (Shimadzu CFT-500 C) under 9.807 MPa. The glass transition and melting temperatures of TIR are reported to be −60°C and 74°C, respectively.[10] Based on these data, for further experiments the MAH-modified TIR (MTIR) was prepared at 150°C and 30–70 rpm for 10 min.

Compounding TIR, MTIR, and WF

Compounding TIR and WF as well as TIR, MTIR, and WF were carried out using a kneader at 100°C, 30 rpm, and 10 min. That is, a prescribed amount of TIR, with or without MTIR, was placed in the kneader at 100°C and 30 rpm for 2 min. The WF was added subsequently over 3 min, and mixing was then continued for 5 min. The total kneading time was 10 min. The amount of matrix and WF were 24 g, which filled the mixing chamber and caused torque while kneading.

Preparation of composite sheet

Kneaded samples were molded into a sheet by hot pressing with Toyoseiki 10-ton bench hot press for testing. The prescribed amount of kneaded sample (5–7 g) was placed between a pair of thick Teflon sheets with a 0.3-mm-thick spacer. The temperature of the hot pressing was 120°C, and the material was subjected to 0–50 and 150 kgf/cm^2 pressures for 2.0 and 0.5 min, respectively. After subsequent cold pressing at the same presssure for 30 s, the sheets were cooled at room temperature.

Tensile test

Strip samples 80.0 × 5.0 × 0.3 mm were prepared from composite sheets. Tensile tests were made on these strip samples with a Shimadzu autograph DCS-R-500. The measurements were made with a span length of 40 mm and a cross head speed of 10 mm/min in a room adjusted to 20°C and 60% relative humidity (RH). The average values for tensile strength, elongation at break, and Young's modulus were obtained from 10 repeated measurements.

Viscosity measurement

A flow tester (Shimadzu CFT-500 C) was used for the melt viscosity measurement. After being dried at room temperature in vacuo for 48 h, approximately 1.0–1.2 g of the kneaded sample was prepared for measurement, which was made at 200°C under a constant load of 100 kgf.

Flow test

Thermal flow temperature of the blended samples was measured by the flow tester. The measurement was made at constant heating rate of 10° C/min under a compressive load of 100 kgf.

Water absorption and thickness swelling test

Square samples of 50.0 × 50.0 × 0.3 mm were prepared from the composite sheets. Water absorption and thickness swelling tests were conducted on these square samples in three replications. The samples were dried overnight in an oven at a temperature of 50°C and were then stored in desiccator. The weight and thickness of the samples were measured in a room adjusted at 20°C and 60% RH. Subsequently, the samples were dipped for 24 h in water that had been conditioned in a room adjusted at 20°C, 60% RH for 48 h. The samples were then wiped, and the weight and the thickness were measured. Finally, the samples were dried in

a 50°C oven to obtain the constant weight. Water absorption and thickness swelling were calculated.

Scanning electron microscopy observation

The morphology of the tensile fracture of the composites after being sputter-coated with gold was studied using a JEOL JSM-T330A scanning electron microscope (SEM). SEM photographs were taken under the following conditions: working distance 15 mm, accelerating voltage 10 kV.

Results and discussion

Mechanical properties of WF–TIR or MTIR composites

To determine the effect of WF concentration on the mechanical properties of TIR–WF and MTIR–WF composites, tensile tests were conducted at various WF concentrations, ranging from 0 to 60%. In this experiment, MTIR prepared from TIR and 20% MAH (MTIR·20) was used. The results are shown in Fig. 1.

The tensile strength of the composite of MTIR and WF becomes greater with increases in the blending proportion of WF up to 50%. Beyond this point, an increase in the WF content reduces the tensile strength of the composites. The composite of MTIR with 50% WF content has a tensile strength of 18.8 MPa, which is 1.2 and 2.4 times greater than that of the composites of TIR without WF and TIR with 50% WF, respectively. Conversely, when TIR is blended with WF, the tensile strength is found to decrease considerably with increases in the WF content. Concerning the breaking elongation value, the two composites had similar tendencies but possess wide differences in the values. The addition of WF up to 20% to the TIR matrix results in a slight decrease in the breaking elongation; further WF addition produces a drastic drop up to 40% WF content. On the other hand, increasing the amount of the WF content in the MTIR matrix drastically decreases the breaking elongation. These results suggest a stronger interfacial interaction or compatibility between the MTIR matrix and WF than in the case of TIR and WF. Another important feature in Fig. 1 is that in both composites a substantial increase in Young's modulus is observed with increasing WF content.

From the above observations, it may be concluded that the WF–MTIR and WF–TIR composites have large differences in their characteristics and mechanical properties. The WF–MTIR composite has enhanced mechanical properties compared to those of TIR with or without WF.

MTIR as a compatibilizer of TIR–WF composites

Mechanical properties of the composites

It is known in general that the use of a compatibilizer for the composite can improve its mechanical properties. Therefore, in this study the MTIR·10 was evaluated as a
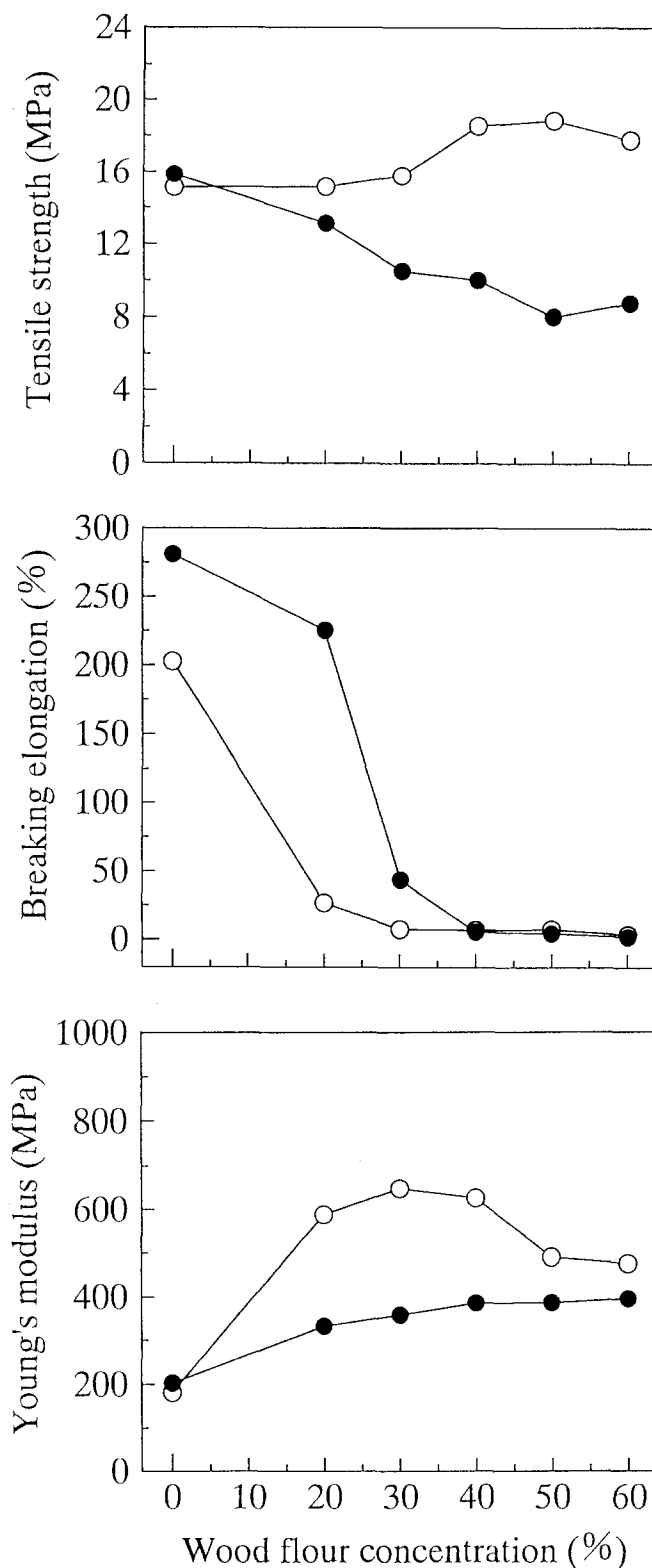
Fig. 1. Relations between wood flour concentration and the tensile properties of *trans*-1,4-isoprene rubber–wood flour composites (TIR-WF) and 20% maleic anhydride (MAH)-modified wood flour (MTIR-20-WF) composites. MTIR is prepared from TIR and 20% MAH. *Open circles*, MTIR-20; *filled circles*, TIR
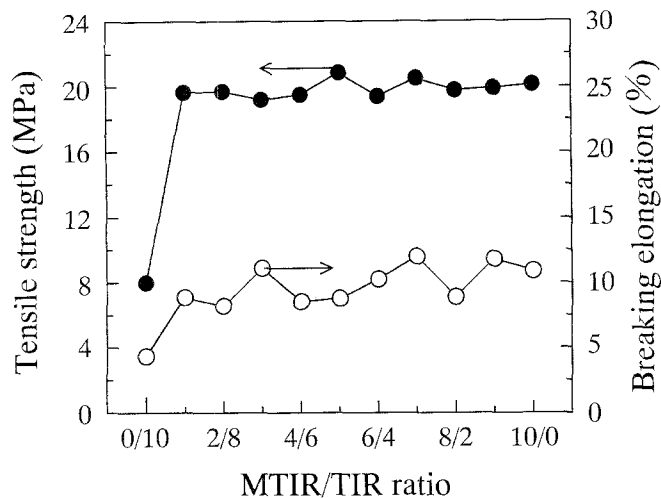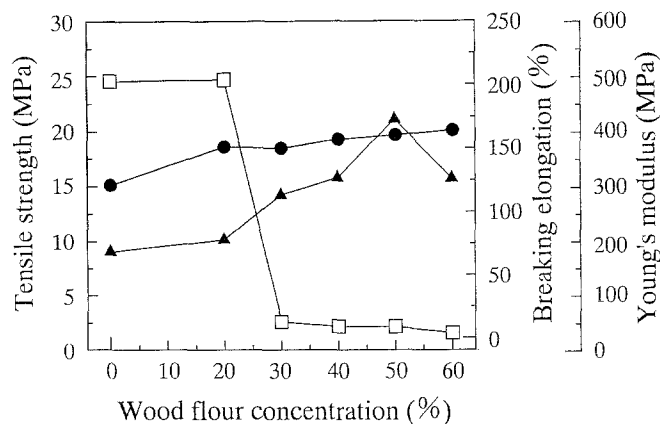
Fig. 2. Relations between the MTIR·10/TIR ratio and tensile strength and the breaking elongation. MTIR is prepared from TIR and 10% MAH. The WF was 50%. *Filled circles*, tensile strength; *open circles*, breaking elongation

Fig. 3. Relations between wood flour concentration and tensile strength, breaking elongation, and Young's modulus of composites. MTIR is prepared from TIR and 10% MAH. The MTIR·10/TIR ratio is 1:9. *Circles*, tensile strength; *squares*, breaking elongation; *triangles*, Young's modulus

compatibilizer to improve the properties of the TIR–WF composite. The tensile properties are presented in Fig. 2.

It is clear that the tensile strength of the composite increases with a small addition of the MTIR. A marked increase is noted up to 5% addition of MTIR to the whole composites, and the tensile strength obtained is 19.7 MPa, which is 2.5 times greater than that of the WF–TIR composite without MTIR. Further addition of the MTIR results in almost no additional improvement. The breaking elongation of the composites with MTIR as a compatibilizer is higher than that of the control composite.

We also measured the tensile properties of the composites made up of TIR and MTIR·10 as a matrix and various concentrations of WF. The weight ratio of TIR and MTIR·10 is 9:1. The WF varied from 0 to 60%. The results are shown in Fig. 3. The tensile strength and Young's modulus of the composite increase with increasing WF concentration. An addition of WF from 20% to 60% results in similar tensile strengths. The maximum tensile strength and Young's modulus obtained are approximately 1.3 and 2.4 times larger than that of TIR – MTIR film without WF. Addition of WF from 20% to 30% drastically decreases the elongation at the break of the obtained composite.

It is known that the strength of the short-fiber composite is dependent on the transfer of load from the matrix to the fiber. Well-developed interactions between WF and the TIR phase are thus required for obtaining the higher tensile strength. These results suggest that MTIR promotes adhesion between the WF and TIR components. It is proposed that the following mechanism is responsible for the enhancement of adhesion: MAH added on the TIR chain is highly reactive toward the hydroxyl group on the WF surface, and when kneading and pressing at elevated temperatures both covalent and hydrogen bonds develop between the compatibilizer and the WF surface. The MTIR then covers the WF surface and wetting is achieved by the TIR

phase. Better contact between WF and TIR is achieved, which results in higher tensile strength and breaking elongation values of the composites.
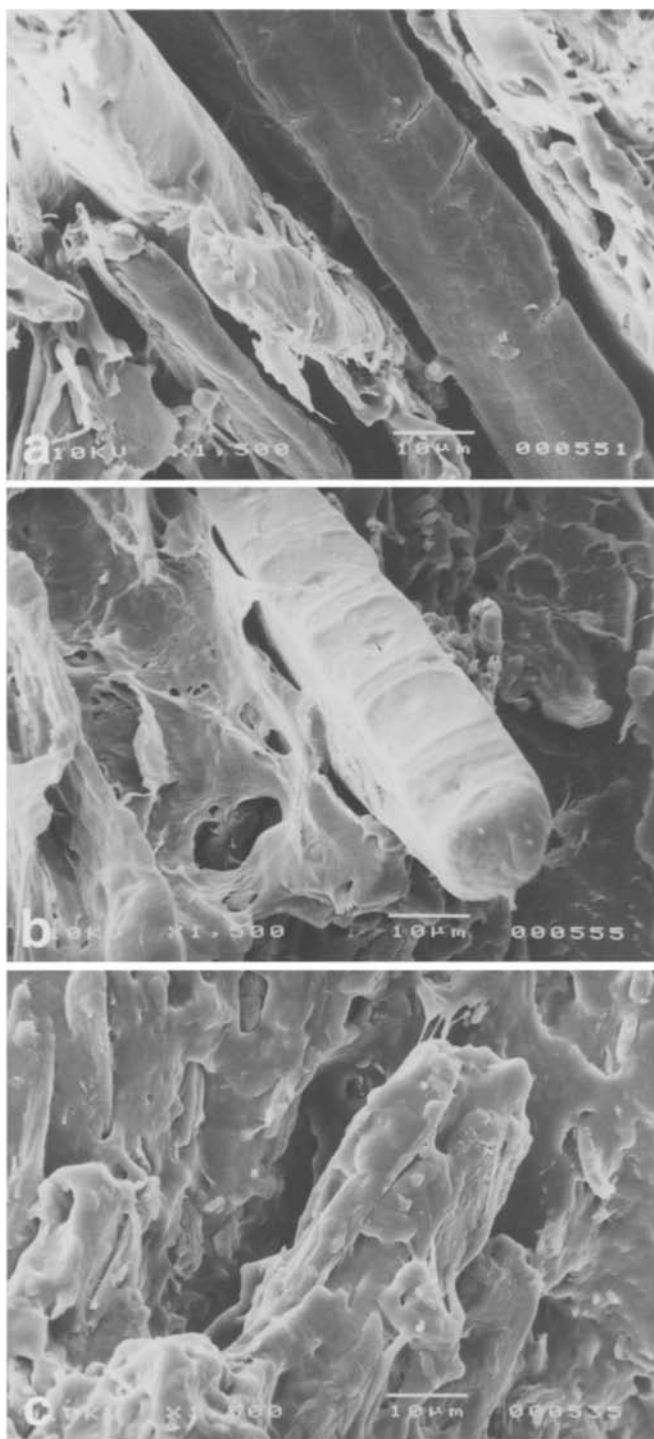
Scanning electron micrographs of the tensile fracture parts of composite samples support this argument. Figure 4 shows the tensile fractures of the composites based on 50% matrix and 50% WF with and without a compatibilizer.

Owing to the hydrogen bonds formed among the WF surfaces and the difference in polar character between the WF and the matrix, the WF tends to agglomerate into bundles and becomes unevenly distributed throughout the matrix (Fig. 4A). Moreover, holes and spaces commonly are formed along the fiber, and the fibers pull out, which indicates insufficient adhesion, very low compatibility, poor contact, and inferior stress transfer between the phases. The use of MTIR as a compatibilizer prevents hydrogen bonds from being formed among the WFs and causes the properties of WF surfaces and the matrix to become more similar. The MTIR compatibilizer facilitates direct contact between the WF fillers and the TIR phase and enhances their dispersion in the TIR phase (Fig. 4B, C). As the entire fibers are covered by layers of the matrix materials, it can be concluded that the contact between the TIR and WF phases is improved by the compatibilizer.

Although the tensile strength of the composite consisting of 50% WF/5% MTIR/45% TIR and that of 50% WF/25% MTIR/25% TIR are similar, increasing the amount of a compatibilizer results in better dispersion and wetting of fibers in the matrix.
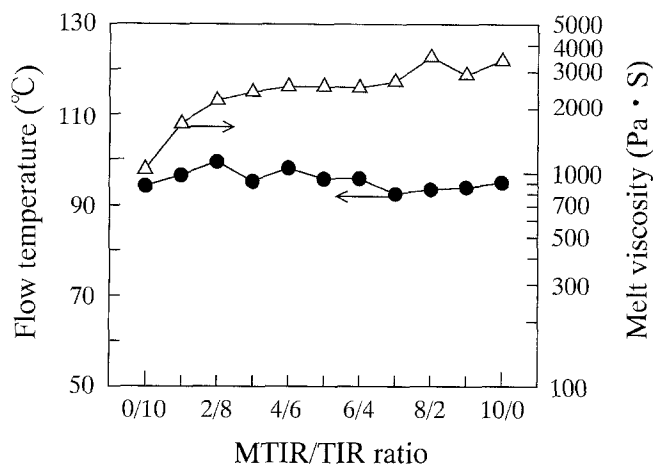
Flow properties of the composites

Understanding and controlling the physicochemical properties of the composites (especially flow temperature) are important for optimizing the processing operation and upgrading the final properties of the composite products. Therefore, the flow characteristics of the TIR–WF composites with or without MTIR compatibilizer were also studied.

Fig. 4. Scanning electron micrographs of the tensile fracture. **a** 50% WF and 50% TIR. **b** 50% WF and 5% MTIR·10 and 45% TIR. **c** 50% WF and 25% MTIR·10 and 25% TIR

Fig. 5. Relations between the MTIR·10/TIR ratio and melt viscosity and the flow temperature of composites. MTIR is prepared from TIR and 10% MAH. WF was 50%. *Triangles*, melt viscosity; *Circles*, flow temperature

The results on the melt viscosity (Fig. 5) show that addition of MTIR to the matrix increases the melt viscosity. In general, the melt viscosities of the polymers are affected by various factors, notably average molecular weight, molecular weight distribution, chain branching, and chemical characteristics of the polymer. The more polar the polymer, the

higher are are the viscosities.[11] In this case, the matrix polymer gain enhanced polarity by a compatibilizer (MTIR) addition. The MTIR can graft onto the hydroxyl group of wood on its surface area through esterification during the processing.[1] It is also presumed that when MAH is attached to TIR crosslinking might occur. If these reactions take place, the melt viscosities of composites enlarge, which also can be caused by adhesion between the matrix and the WF.
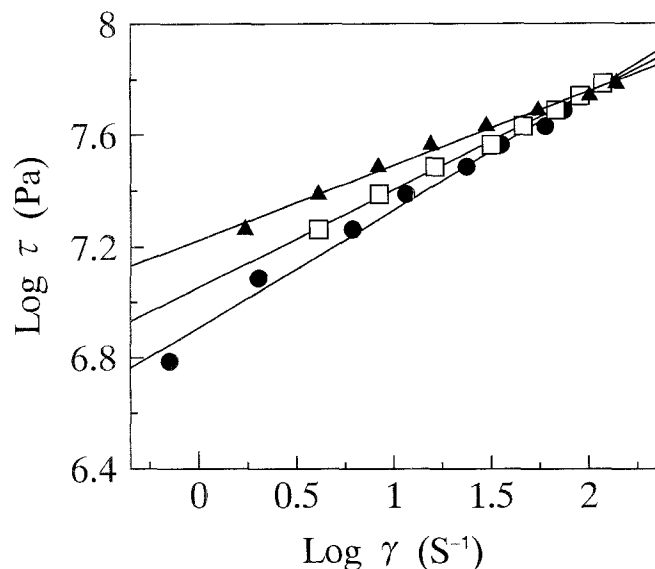
Compared to the flow temperature of the control composites, addition of the MTIR as a compatibilizer onto the matrix gave the products with very similar flow temperatures. The highest flow temperature obtained was 99.6°C, which is the case for the composites with 20% MTIR compatibilizer.

The flow temperature and melt viscosity of the composite increase with increasing WF concentration. The higher the WF concentration, the higher are the flow temperature and the melt viscosity of the composite obtained (Fig. 6). This phenomenon can be attributed to the lubricating of the wood fiber. In general, in the high filler-loading composites, the filler–filler interactions become the dominant factor affecting the rheology of the filled melt, especially in the case where the filler has large polarity. At high loads, the close proximity of the filler leads to strong filler–filler interactions that increase with an increase in the polarity of the filler. The strong filler–filler interaction can result in severe agglomeration of fillers. Under this circumstance, the lubricating of filler surface is predominant not only to diminish the agglomeration of fillers but also to promote slippage between matrix and filler, which results in significant improvement on the rheology of filled melt.[12]

The apparent flow curves, shear stress τ versus shear rate γ plots for the composite melts with or without compatibilizer under a constant temperature, are shown in Fig. 7. All the flow curves are linear in the studied range of shear rate, suggesting that the flow of the composite melts is shear thinning and obeys the Ostwald de Waele power laws.
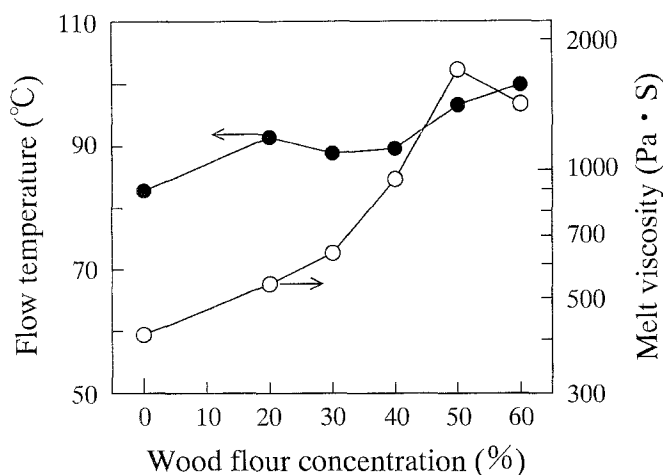
Fig. 6. Relations between wood flour concentration and the flow temperature and melt viscosity of composites. MTIR was prepared from TIR and 10% MAH. MTIR·10/TIR ratio was 1:9. *Open circles*, melt viscosity; *filled circles*, flow temperature

Table 1. Values of power law exponent n and zero shear viscosity

MTIR/TIR/WF ratio	n	$\eta_0 \times 10^{-4}$ (Pa·S)
0/50/50	0.422	8.14
5/45/50	0.349	11.14
50/0/50	0.266	16.88

Fig. 8. Plots of log η vs. log γ for TIR–WF; TIR–MTIR·10–WF, and MTIR·10–WF composites. MTIR was prepared from 10% MAH. The WF was 50%, and the temperature of the measurement was 100°C. *Circles*, MTIR·10/TIR, 0:10; *squares*, MTIR·10/TIR, 1:19; *triangles*, MTIR·10/TIR, 10:0
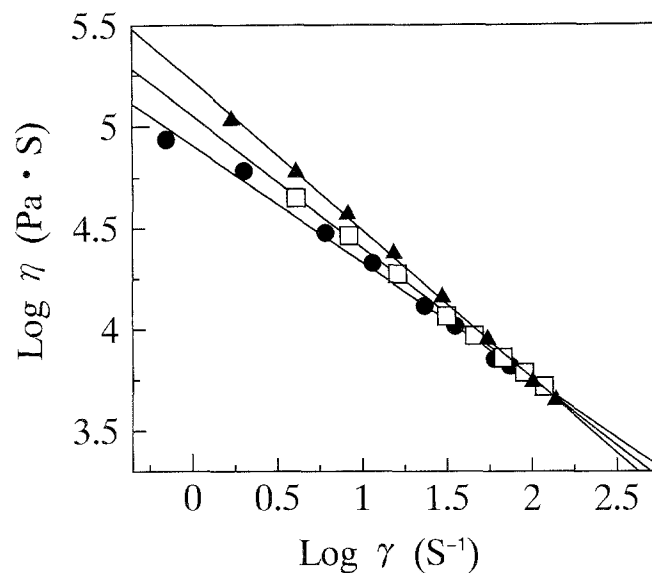

Fig. 7. Plots of log τ vs. log γ for TIR–WF, TIR–MTIR·10–WF, and MTIR·10–WF composites. MTIR was prepared from 10% MAH. WF was 50%, and the temperature of the measurement was 100°C. *Circles*, MTIR·10/TIR, 0:10; *squares*, MTIR·10/TIR, 1:9; *triangles*, MTIR·10/TIR, 10:0

$$\tau = \eta\gamma = k\gamma^n$$

where η is the apparent viscosity; γ is the shear rate; τ is the shear stress; k is the shear viscosity coefficient; and n is the power law exponent. The values of the power law exponent n is evaluated by regression analyses.

As can be seen in Table 1 the values of n for the composite TIR–WF with or without MTIR compatibilizer are less than unity and decrease with addition of MTIR compatibilizer. Addition of 5% MTIR compatibilizer decreases the n value from 0.422 to 0.346; further decrease can be found by increasing the amount of MTIR compatibilizer.

Figure 8 reveals the melt viscosities (η) of the TIR–WF composites with or without MTIR compatibilizer as a function of shear rate (γ) at a constant temperature. It is clear that log η decreases linearly with increasing log γ, indicating that the dependence of η on γ also obeys the power law equation. The variation of slopes for the plots, log η versus log γ, with an addition of the MTIR compatibilizer, is consistent with the variation of n values mentioned above, indicating that the higher the amount of MTIR, the more sensitive is η to γ. Based on these findings, it can be said that the composite of TIR–MTIR–WF melts are of pseudoplastic nature. The pseudoplastic nature of these composites can be explained as follows: when the particles in a dispersion come into contact, links are formed. Under the influence of shear these links are stretched and distorted, and they rupture. Therefore, the viscosity decrease with the increase in shear rate.[13,14] The degree of the pseudoplasticity increases with the increase in the amount of MTIR compatibilizer in the composites. As for the zero shear viscosity, it shows a clear tendency to increase with the increase in the amount of MTIR (Table 1).

Figure 9 shows the plot of log η versus $1/T$ obtained under a constant shear stress. Under the measured range of shear stress, the apparent viscosities of the TIR–WF
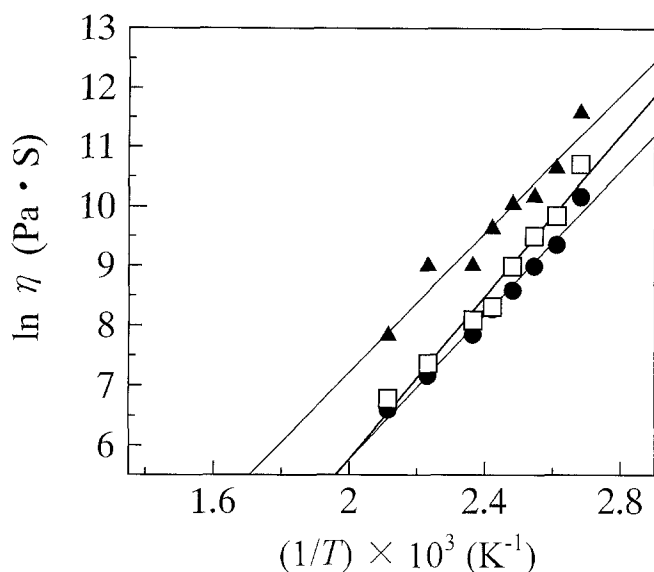
Fig. 9. Plots of log η vs. 1/T for TIR–WF, TIR–MTIR·10–WF, and MTIR·10–WF composites. MTIR was prepared from 10% MAH; WF was 50%. Shear stress, 2.451 × 10^6 dyne/cm^2. *Circles*, MTIR·10/TIR, 0:10; *squares*, MTIR·10/TIR, 1:9; *triangles*, MTIR·10/TIR, 10:0

Table 2. Values of activation energy for melt flow

| MTIR/TIR/WF ratio	Activation energy (kJ/mol)
0/50/50	48.8
5/45/50	56.3
50/0/50	42.8

composite melts with and without MTIR compatibilizer decrease linearly with increasing temperature, indicating that the dependence of η on temperature obeys the Arrhenius equation:

$$\eta = A\exp(E/RT)$$

where A is a constant that is related to material properties; E is the activation energy for flow; R is the universal gas constant; and T is the absolute temperature. The activation energies of the composites were calculated based on the above equation, and the results are presented in Table 2. The activation energy of the TIR–WF composite with 5% MTIR compatibilizer has higher activation energy for flow compared to that of the TIR–WF composite but decrease further with increasing MTIR content. Addition of a small amount of MTIR compatibilizer leads to an increase in hindrance of molecular motion.

Water absorption and thickness swelling of the composites

Utilization of MTIR as a compatibilizer markedly improves the tensile strength of composites. In addition, certain physical properties, including water absorption and thickness swelling of the composites composed of TIR, MTIR, WF, were measured.
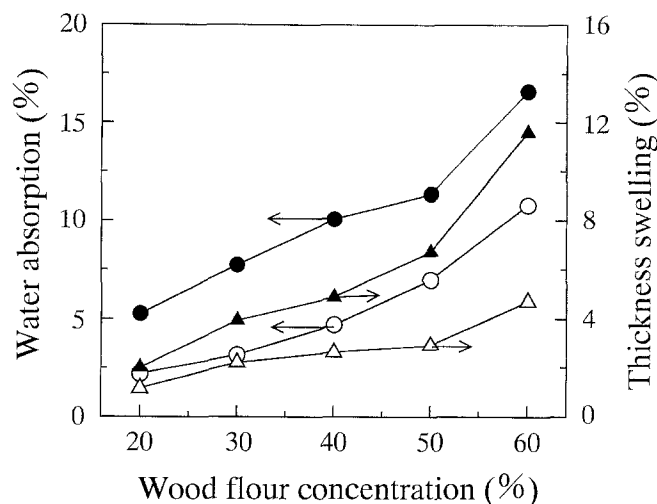
Fig. 10. Relations between wood flour concentration and the water absorption and thickness swelling of composites. MTIR was prepared from 10% MAH. *Filled symbols*, TIR; *open symbols*, MTIR·10/TIR, 1:9

Because of the existence of hydroxyl groups, one of the disadvantages of wood and wood composite products is the dimensional instability. As shown in Fig. 10, the composites with MTIR absorb considerably less water than the composites without it. In this experiment the presence of MTIR as a compatibilizer in the composites obviously improves these physical properties. The absorption of water by TIR or MTIR, which is hydrophobic in nature, is negligible. As a result, the increase in water absorption and thickness swelling are proportional to the concentration of WF in the composites. The water-repellent property and higher dimensional stabilization are attained by grafting WF with MTIR through esterification.[1] That is, it is possible for esterification to occur during kneading at 100°C for 10 min, followed by hotpressing at 120°C for 2.5 min. This might be one of the reasons that adhesion between the TIR matrix and WF is enhanced, giving high waterproof properties compare to that in the controls.

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