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Tensile Properties and Dimensional Stability of Wood Flour–Reinforced cis–1,4–Isoprene Rubber Composites

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Wood flour (WF)–reinforced cis–1,4–isoprene rubber (CIR) composite was prepared through a melting process. Maleic anhydride (MAH), dicumyl peroxide (DCP), and zinc oxide (ZnO) were added to the composites to enhance their tensile properties and dimensional stability. The dependence of MAH, DCP and ZnO concentration at various pressing time on tensile strength, elongation at break, Young’s modulus, water absorption (WA) and thickness swelling (TS) of WF–CIR composites were examined. The tensile strength, elongation at break, and Young’s modulus of the WF–CIR were greatly influenced by MAH content and pressing time. The higher the MAH concentration and the longer time were applied, the greater improvement of tensile strength, Young’s modulus, water absorption and thickness swelling parameters were obtained. However, the elongation at break was found to decrease with addition of MAH. DCP and ZnO concentration were also influenced the tensile strength, elongation at break and Young’s modulus for WF–CIR composites.

Key words: cis–1,4–isoprene rubber, composites, dicumyl peroxide, maleic anhydride, wood flour

INTRODUCTION

Polysisoprene (natural rubber and synthetic polyisoprene) can be modified by the following methods: (i) grafting with random addition of unsaturated monomers (e.g., MAH, acrylonitrile, etc.), (ii) chemical reactions such as the formation of aldehydes and thio derivatives, and (iii) partial isomerization reactions such as halogenation and hydrohalogenation (Hofmann, 1989). It has been reported that maleic anhydride (MAH) can be easily introduced into trans–1,4–isoprene rubber (TIR) without the use of any peroxides to form MAH–modified–TIR (MTIR). This copolymer (MTIR) can further react with the hydroxyl (OH) groups of wood flour (WF) and corn starch (CS) fillers, and has been successfully used as a compatibilizer for WF–MTIR or CS–MTIR composites (Febrianto et al., 1999; 2001). It can also be used as a hot–melt adhesive in plywood manufacturing (Febrianto et al., 2006).

Compared to TIR, cis–1,4–isoprene rubber (CIR), which is more abundant (both in nature and the polymer industry) and relatively inexpensive, has a lower melting temperature. In general, easily masticated CIR capable of being blended with fillers, processing aids, activators, antioxidants, and curing agents provides final commodity products by using conventional techniques in thermoplastic manufacturing (Hofmann, 1989). Fiber–reinforced rubbers are of considerable practical and economical interest to the rubber industries because of their potential for simplifying the molding and manufacturing of reinforced–rubber products such as hoses and conveyor belts (Ahlblad et al., 1994).

Two of the most important prerequisites in composite manufacturing are obtaining a good fiber dispersion and adequate interfacial adhesion between the fiber and the matrix. However, the reinforcement depends on the size, surface chemistry, state of aggregation, and quantity of filler material. The dispersion of wood fibers in polyisoprene matrix using a combination of MAH and peroxides has rarely been reported. The mechanical properties, water absorption, and curing characteristics of natural rubber (NR)–WF composites are significantly influenced by the WF content and particle size (Hong et al., 2011; Ichazo et al., 2006).

To the best of our knowledge, the research on WF–reinforced plastic composite using CIR as a matrix polymer have rarely conducted, particularly using combination of MAH and DCP. In this study, the effects of the additives—(i) MAH as a modifier under various pressing times, (ii) dicumyl peroxide (DCP) as a crosslinking agent, and (iii) zinc oxide (ZnO) as an antioxidant—on the physical and mechanical properties of WF–CIR composites were investigated.

MATERIALS AND METHODS

Materials

WF of 200 mesh–pass size was obtained from Hitachi

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Chemical Co. (Tokyo, Japan). It was dried in an oven at 105°C for 24 h, and then kept in a desiccator at room temperature before use. CIR, used as the matrix polymer, was obtained from Japan Synthetic Rubber Co. Ltd. (Tokyo, Japan). MAH, DCP, ZnO, and stearic acid (SA) were obtained from Nacalai Tesque Inc. (Kyoto, Japan) and used without any further purification.

Preparation of composites and sheets
The mass ratio of WF:CIR was set at 1:1. A prescribed amount of CIR was placed in a kneader (Labo Plastomil LPM 18–125, Toyo Seiki Co. Ltd.). The temperature, rotation rate, and mixing time were set at 90°C, 30 rpm, and 2 min, respectively. Then, MAH, DCP, ZnO, and SA were added to the kneader with simultaneous kneading for another 2 min before WF was continually added to the mixture for the next 3 min, finally followed by more kneading for 5 min. The total kneading time was 12 min.

The kneaded samples were molded into sheets by a hot press using Toyo Seiki 10 T Bench. The prescribed amount of kneaded sample (5–7 g) was placed between a pair of 2 mm–thick Teflon sheets with a 0.4 mm–thick spacer. The temperature of the hot press was set at 160°C, and the samples were subjected to 9.81 N mm$^{-2}$ pressure. The pressing time was 5–25 min. After subsequent cold pressing of the hot–pressed sheets at the same pressure for 30 s, they were cooled to room temperature.

Determination of tensile properties
Ten strip samples of 80×5×0.4 mm size were cut from the hot–pressed sheets, and their tensile strengths were measured using a Shimadzu Autograph DCS–R–500 (Kyoto, Japan). The measurements were performed with a span length of 40 mm and a crosshead speed of 10 mm/ min under the ambient temperature and relative humidity (RH) adjusted to 20°C and 60%, respectively. The average values of tensile strength, elongation–at–break, and Young’s modulus were obtained from the results of the tests of the ten samples.

Determination of water absorption and thickness swelling
Square samples of 50×50 mm$^2$ having 0.3 mm in thickness were prepared from the composite sheets. The water absorption (WA) and thickness swelling (TS) tests were carried out on three specimens above prepared. The samples were dried overnight in a vacuum oven at 60°C and then stored in a desiccator. The thickness (T1) of samples was measured at 20°C and 60% RH. The samples were then dipped in water for 24 h, which was pre–conditioned for 48 h to set–up at 20°C and 60% RH, respectively. After the samples were wiped, their weight and thickness (W2 and T2) were measured. Finally, the samples were dried in a vacuum oven at 60°C until reached a constant weight (W3). The WA and the TS were calculated as shown in the following equation.

$$WA = \frac{W_2 - W_3}{W_3} \times 100\%$$

$$TS = \frac{T_2 - T_1}{T_1} \times 100\%$$

RESULTS AND DISCUSSION
Dependence of MAH concentration and pressing time on tensile properties and dimensional stability
The mass ratio of WF to CIR was set to be 1:1, and the amounts of DCP, ZnO, and SA were fixed at 3%, 5%, and 1% of the total mixture basis, respectively. The amount of MAH was varied from zero to 40% in the basis of CIR weight. The pressing times were set at 5, 15, and 25 min. Under such conditions, the tensile strength, WA, and TS of the resulting composites were investigated. The results are summarized in Fig. 1–3.

Fig. 1 shows the significant effects of MAH concentration and pressing time on the tensile strength of WF–CIR composites. The dependence of MAH concentration and pressing time on the Young’s modulus of the CIR–WF composites is shown in Fig. 2.

Fig. 1. Dependence of maleic anhydride (MAH) concentration and pressing time on the tensile strength of CIR–WF composites.

Fig. 2. Dependence of MAH concentration and pressing time on the Young’s modulus of the CIR–WF composites.
WD-Flour-Reinforced Rubber Composites

The addition of MAH to the WF-CIR composites enhanced their tensile strength. Fig. 1 shows that without MAH, the WF-CIR composite with certain amounts of DCP, ZnO, and SA showed similar values (~4 MPa) at different pressing times. The addition of MAH up to 10% slightly improved the tensile strength. A higher pressing time resulted in a greater tensile strength. When the MAH concentration was increased from 10% to 20%, the corresponding tensile strengths were drastically increased, particularly at 15 and 25 min pressing times. Beyond this MAH concentration, the tensile strength of WF-CIR composites improved slightly and reached its maximum value at 30% MAH concentration (remarkable for treatments at pressing time: 15 and 25 min). On the other hand, concerning samples at 5 min pressing time, the tensile strength increased gradually with increasing MAH concentration, and reached its maximum value at 40% MAH concentration. However, the maximum values of tensile strength were significantly distinguished among the three systems at different pressing time.

Fig. 2 shows the significant effects of MAH concentration and pressing time on the Young’s modulus of the WF-CIR composite, wherein a trend similar to that exhibited by the tensile strength was observed. Without added MAH, the Young’s modulus of the WF-CIR composite (with certain amount of DCP, ZnO, and SA) showed similar values even at different pressing times. A prolonged pressing time (from 5 to 15 min or more) resulted in a slight increase in Young’s modulus. Then, the value of Young’s modulus increased slightly up to 20% MAH concentration. Longer pressing times resulted in greater Young’s modulus. By increasing the MAH concentration from 20% to 30%, a drastic enhancement in Young’s modulus was observed, particularly at 15 and 25 min pressing time. Beyond this point, the Young’s modulus increased slightly with increasing MAH concentration. The highest Young’s modulus value was obtained at 40% MAH concentration in each treatment at different pressing times. Similar changes in the Young’s moduli of the WF-CIR composite were observed at MAH concentrations ≥ 20% at 15 and 25 min pressing times. These Young’s moduli were significantly different from those at 5 min pressing time.

Fig. 3 shows the positive influence of MAH concentration and pressing time on elongation–at–break of the WF-CIR composites. Without addition of MAH, the elongation–at–break of the WF-CIR composites (with certain amount of DCP, ZnO, and SA) at 5 min pressing time exhibited the highest value when compared with other systems at 15 and 25 min pressing time. Almost identical values at elongation–at–break in WF-CIR composites appeared for the two systems at 15 and 25 min pressing times. The elongation–at–break of the WF-CIR composite samples at 15 and 25 min pressing times were not significantly changed through the MAH concentration measured, when compared with the drastic changes at 5 min pressing time, which was a remarkable decrease in the elongation–at–break by the addition of 2.5–5% MAH onto the WF-CIR composites, prior to a gradual decrease at 10% MAH concentration started. Finally it reached a minimum value similar to those in the range of 30–50% for the other two systems at 40% MAH concentration.

The increase in Young’s moduli and decrease in elongation–at–break of the WF-CIR composites, with certain amounts of added DCP, ZnO, and SA and no MAH addition as above described, are presumably due to the peroxide vulcanization of CIR in the presence of DCP (Hofmann, 1989). Furthermore, the increase in tensile strength and Young’s moduli and the decrease in elongation–at–break of the WF-CIR composite, with certain added amounts of DCP, ZnO, SA, and MAH, could presumably be attributed to the reaction of MAH with the CIR matrix, as characterized by the esterification between the anhydride groups of MAH and the OH groups of the PD during kneading, and the crosslinking of CIR by DCP. A longer pressing time resulted in a higher cross–linked density of CIR. Based on this study, the optimal condition to develop WF–CIR composites with certain amounts DCP, ZnO, and SA was obtained by the addition of 30% MAH and at 25 min pressing time. The tensile strength, elongation–at–break, and Young’s modulus of the WF–CIR composite were calculated as 12.70 MPa, 22.00%, and 138.70 MPa, respectively.

It has been demonstrated that the presence of 30% MAH induced increases in the tensile strength and Young’s modulus of the WF-CIR composites. A similar phenomenon was observed for the WA and TS properties as shown in Fig. 4. It is clear that both the WA and TS values were unchanged by the addition of 2.5% MAH to the WF–CIR composite. The WA and TS values significantly dropped when the MAH concentration was increased up to 5%. The WA value decreased when the MAH concentration was increased further up to 10%. Beyond this point, both the WA and TS values remained constant.

One of the disadvantages for all wood and wood–based composite products is their dimensional instability. This is mostly attributed to the existence of OH groups that allows easy access of water vapors. It is
apparent that the values of WA and TS were significantly influenced by the MAH concentration. The WA and TS values of the WF–CIR composites without MAH were found to be 13.0 and 8.0%, respectively. The lowest WA (7.7%) and TS (4.0%) values were obtained from the WF–CIR composites with 30% MAH concentration. The presence of MAH in the WF–CIR composites had clearly improved their WA and TS values. The esterification (between the anhydride groups of MAH and OH groups of WF) and crosslinking (of rubber with DCP) have restricted the composites from absorbing water, and this led to the reduction of WA and TS values as compared to the control experiment (Fig. 4). A similar phenomenon was reported by Febrianto et al. (1999; 2001) when reacting WF and TIR in the presence of MAH.

Effect of ZnO concentration on the tensile properties of WF–CIR composites

Like all the elastomers, synthetic polyisoprene also requires the addition of an activator to promote a faster overall rate for cure and higher final crosslinking density (Hofmann, 1989). Therefore, the effect of the amount of added activator (ZnO) on the tensile strength, elongation–at–break, and Young’s modulus of the composites comprised of 100 parts of CIR, 100 parts of WF, 30 parts of MAH, 5 parts of DCP, and 1 part of SA by weight were determined. The ZnO content in the composites was varied from 1 to 5 parts by matrix weight. The results are summarized in Fig. 5.

Fig. 5 shows the dependence of ZnO addition on the tensile strength, elongation–at–break and Young’s modulus of the WF–CIR composites. It is apparent that an increase in the ZnO concentration up to 3% significantly enhanced the tensile strength and Young’s modulus; however, it did not provide a significant effect on the elongation–at–break of the WF–CIR composites. Addition of ZnO at more than 3% resulted in a decrease in the tensile strength and Young’s modulus of the WF–CIR composites. Evidently, the tensile properties of the WF–CIR composites cross–linked with DCP was enhanced by the presence of ZnO, due to a faster overall rate of cure and a higher final crosslinking density (Hofmann, 1989). In this experiment, the addition of 3% ZnO was an effective amount to enhance the crosslinking density in the WF–CIR composites.

Effect of DCP concentration on the tensile properties of WF–CIR composites

Crosslinking rubber with peroxides has been known for a long time, and it supplements to the conventional sulfur–vulcanization method. Because of the heat stability resulting from peroxide vulcanization, this type of vulcanization has achieved a great importance. DCP is a peroxide without any carboxylic acid groups. Compared to peroxides with carboxylic acid groups, DCP has the following characteristics: sensitive to acids, possess higher decomposition temperature, and less sensitive to oxygen (Hofmann, 1989). In the present study, the effect of DCP concentration on the tensile strength, elongation–at–break, and Young’s modulus of WF–CIR composites comprised of 100 parts of CIR, 100 parts of WF, 30
parts of MAH, 3 parts of ZnO, and 1 part of SA were determined. The DCP concentration was varied from zero to 10% based on the CIR weight. The results obtained are presented in Fig. 6.

Fig. 6 shows the effect of ZnO addition on the tensile strength, elongation–at–break, and Young’s modulus of the WF–CIR composites. It is concluded that the tensile strength, elongation–at–break, and Young’s modulus of the CIR–WF composites were greatly influenced by the DCP concentration. A higher DCP concentration of up to 8% resulted in a greater tensile strength of the WF–CIR composites, and it remained constant beyond this concentration. The value of Young’s modulus slightly increased for up to 5% DCP addition, before it significantly increased when the DCP concentration was increased up to 8%. Beyond this concentration, the Young’s modulus of the WF–CIR composites decreased. On the other hand, the addition of DCP onto the WF–CIR composites was found to decrease its elongation–at–break. When the amount of DCP was increased from 1 to 5%, it resulted in a significant decrease in the value of elongation–at–break. Then the elongation–at–break was almost saturated at 10% with increasing DCP concentration of up to 8%. The degree of crosslinking achieved in peroxide vulcanization primarily depends on the type and amount of peroxide, radical yield, and the reactivity of the rubber. Furthermore, the radical yield and crosslinking density depends on the temperature in general. The maximum cure temperature of DCP was reported to be 170˚C (Gaylord and Mishra, 1983; Hofmann, 1989). By kneading at 90˚C and pressing at 160˚C for 25 min, superior WF–CIR composites can be produced. The values of tensile strength, elongation–at–break and Young’s modulus were found to be 21.76 MPa, 10.90%, and 649 MPa, respectively.

CONCLUSIONS

It can be concluded that the presence of MAH significantly increased the tensile strength and Young’s modulus, while it decreased the elongation–at–break, WA, and TS of the WF–CIR composite. The tensile strength, elongation–at–break, and Young’s modulus of the WF–CIR composites were also affected by the pressing time, ZnO content, and DCP concentration. The WF–CIR composites prepared from a combination of 30% MAH, 3% ZnO, and 8% DCP (based on the CIR weight), with a compressing time of 25 min showed the better improvements in tensile properties, resulting in values of tensile strength, elongation–at–break, and Young’s modulus of 21.76 MPa, 10.90%, and 649 MPa, respectively.

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