Effect of Filler Shape on Mechanical Properties of Rigid Polyurethane Composites Containing Plant Particles

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Summary: The effect of types of fillers on mechanical properties of rigid polyurethane composite samples was investigated. Polyurethane (PU) composites were prepared using a molasses polyol (MP, a mixture of molasses and polyethylene glycol, Mw=200) diphenylmethane diisocyanate (MDI) and fillers. The following plant particles, bamboo powder, roast bamboo powder, wood meal, coffee grounds, ground coffee bean parchment and cellulose powder, were used as fillers. The mixture of MP and fillers was reacted with MDI by adding an adequate amount of acetone as a solvent. The content of fillers was defined as the ratio of filler weight to total weight of polyol and fillers. The filler content was varied from 10 to 90 wt%. Polyurethane (PU) composites were prepared using fillers with MP. Lengths of major axis and minor axis for each particle regarded as an ellipse were measured using an optical microscope. Averages of diameter and aspect ratio were derived for each plant particle. The relationships between these average values and the mechanical properties, such as strength and elastic modulus, determined by the compression tests were investigated. The effect of filler content was estimated using the apparent volume ratio which is determined as the ratio of the apparent volume of fillers to the reciprocal values of the apparent density of samples. The master curves of the relationships between the specific values of mechanical properties and the apparent volume ratio were obtained. It was found that the compression strength and the elastic modulus for composite samples with different fillers showed maximum values at average aspect ratio around 3. It was also found that the apparent volume ratio, where the mechanical properties showed maximums, decreases with increasing aspect ratio. Using master curves, it is possible to evaluate the mechanical properties of plant particle filled polyurethane composites are described.

Keywords: composites; mechanical properties; molasses polyol; plant fillers; polyurethanes

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Introduction

Composite materials consisting of polymer matrix and fillers are used in various industrial fields, such as car manufacture, construction, aerospace industry, sports equipment, etc., since they are lightweight, easy to process and corrosion resistant. Ordinarily inorganic fillers, such as glass fibers and carbon fibers are used for these composites. The interaction between the fillers and matrix strongly affects the physical properties of composites. Therefore, the fillers are sometimes chemically treated in order to strengthen the adhesion between the surface of the fillers and matrix. These chemical treatments will make industrial products to be more expensive because of the additional processes. Polymer composites are difficult to dispose, because they have high durability, indeed they were developed as materials for the aerospace field.

Polyurethanes derived from saccharides and lignin were extensively investigated in our research group [1-11]. Polyurethanes filled with plant particles were also studied in our group as biodegradable polymer composites [8-11]. The above polyurethane composite samples show excellent physical properties such as thermal and mechanical properties, and also biodegradability [3, 8-11]. These properties make it possible to use them in buildings, such as the interior of walls and floors, and as heat insulating materials. They are also easily disposed after use. At the same time, they show better compatibility between fillers and matrices than those of the ordinary polymer matrix composites, since both fillers and matrix of these composites are derived from plants. Recent legislation concerning the protection of the environment requires the use of natural resources, appropriate cost performance and suitable functionality [12]. For the above composites, the source materials are natural plant wastes, the process of their manufacturing is easy and their physical properties are excellent for building materials. These facts indicate that these composites agree well with the above suggestions.

The mechanical properties of the above polyurethane composites were investigated using the samples filled with various kinds of particles from plant wastes [8-10]. It was found that the mechanical properties, such as strength and elastic modulus, showed the maximum at an adequate amount of fillers [8-10]. However, the values of maximum strength, maximum modulus and also adequate filler content, depended on plant species [8-11]. The filler shape also affects the physical properties of the composites. The effect of filler type on the mechanical properties of the rigid polyurethane composites was investigated in this paper.

Experimental

Materials

A molasses polyol (MP) solution was used as a polyol system for PU composites. MP consists of molasses from sugar cane (Tropical Technology Center Co. Ltd.) and polyethylene glycol (PEG-200). The ground plant particles, such as bamboo powder, roast bamboo powder, coffee grounds, ground coffee bean parchment, wood meal and cellulose, were used as fillers for PU composite samples.

Filler shape observation

Fillers used for composite samples were observed by the optical microscope. Both lengths along the principal axis and perpendicular to the principal axis were measured by regarding the filler shape as an ellipse. For each kind of fillers, the length along the principal axis, and the aspect ratio, which is the ratio of the length along the main axis to the length perpendicular to the principal axis were averaged over 50 filler particles.

Sample preparation

PU composites were prepared by the following procedure [8]. MP was mixed with fillers at various mixing ratios from 10 to 90 wt %, where the mixing ratio was defined as a ratio of filler weight to total weight of MP and fillers. These mixtures were reacted with diphenylmethane diisocyanate (MDI) in the presence of an adequate amount of acetone, which was used as a solvent in order to reduce the viscosity of the mixtures. The solutions were poured into molds and were dried at room temperature for 3 days. After drying, the samples were removed from the molds and cured at 120°C for 2 hours.

Apparent density measurement

The apparent density, ρ_a (gcm^{-3}), was determined as the ratio of sample weight to the apparent volume of cubic samples. The apparent density of fillers, ρ_f (gcm^{-3}), was calculated as the ratio of filler weight to the filler volume.

Mechanical test

The mechanical properties were investigated by compression test [8]. The compression tests were carried out using cubic specimens at a stress rate lower than 10 MPa/min. The compression strength, σ_c (MPa), was determined by the maximum stress in the elastic region, that is, the stress at the end point of the linear part of stress-strain curve from the compression test. The compression modulus, E_c (MPa), was defined as the gradient of the linear part of stress-strain curve. The specific strength, σ_{cs} (MPa $g^{-1}cm^3$), and the specific modulus, E_{cs} (MPa $g^{-1}cm^3$), were calculated as σ_c and E_c divided by the apparent density of samples, ρ_a.

Definitions

The following notations are used in this paper.

f_c: filler content (%)

$$f_c = \frac{W_f(\text{weight of fillers})}{W_f + W_{MP}(\text{weight of molasses polyol})} \times 100 \quad (\%) \tag{1}$$

w_f: weight fraction of fillers (%)

$$w_f = \frac{W_f}{W_f + W_{MP} + W_{ISO}(\text{weight of isocyanate})} \times 100 = \frac{W_f}{W_{sample}} \times 100 \quad (\%) \tag{2}$$

where W_{ISO} is calculated using the mixing index of [NCO]/[OH], [NCO] value of isocyanate and [OH] value of molasses polyol.

ρ_a: apparent density of samples (g cm^{-3}),

$$\rho_a = \frac{W_{sample}(\text{weight of sample})}{V_{sample}(\text{volume of sample})} \quad (\text{g cm}^{-3}) \tag{3}$$

ρ_f: apparent density of fillers (g cm^{-3}),

$$\rho_f = \frac{W_{sample}(\text{weight of fillers})}{V_{sample}(\text{volume of fillers})} \quad (\text{g cm}^{-3}) \tag{4}$$

ρ_{fe}: estimated apparent density of fillers (g cm^{-3}), which is determined by extrapolation from the experimental data.

v_{fa}: apparent volume ratio of fillers (%),

$$v_{fa} = \frac{w_f \times \rho_a}{\rho_f} = {w_f}/{\rho_f} \div {1}/{\rho_a} = \frac{\text{(apparent volume of fillers in sample)}}{\text{(apparent volume of sample)}} \times 100 \quad (\%) \tag{5}$$

σ_c: compression strength (MPa),

E_c: compression elastic modulus (MPa),

σ_{cs}: specific compression strength (MPa $g^{-1}cm^3$),

$$\sigma_{cs} = \frac{\sigma_c}{\rho_a} \quad (\text{MPa g}^{-1}\text{cm}^3) \tag{6}$$

E_{cs}: specific compression modulus (MPa $g^{-1}cm^3$),

$$E_{cs} = \frac{E_c}{\rho_a} \quad (\text{MPa} \cdot \text{g}^{-1}\text{cm}^3) \tag{7}$$

Results and Discussion

The relationship between weight fraction of fillers, w_f, and the apparent density of composites, ρ_a, is shown in Figure 1. At w_f =100% ρ_a represents the apparent density of fillers, ρ_f. ρ_a increases in the initial stage, reaches the maximum and then decreases. As shown in the figure, the maximum values of ρ_a and w_f at maximum ρ_a's are affected by the filler type. Similar relationships between the mechanical properties, such as σ_c, E_c, and weight fraction of fillers, w_f, were obtained. That is to say, σ_c and E_c show the maximum at the optimum values of w_f.

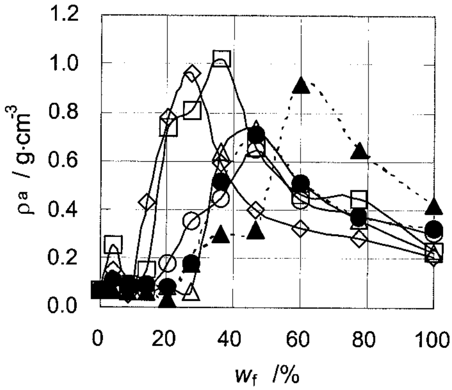


Figure 1. Relationship between weight fraction, w_f, and apparent density, ρ_a; O bamboo powder, ● roast bamboo powder, ▲ coffee grounds, Δ ground coffee bean parchment, ◊ wood meal, □ cellulose [8].

It is known that the mechanical properties of particle-filled composites are always explained by apparent volumes. Therefore, the reciprocal values of apparent density, which are related to the apparent volume, were calculated. The relationship between the reciprocal value of the apparent density, $1/\rho_a$, and w_f for the sample containing bamboo powder is shown in Figure 2. In order to magnify the region of w_f from 40 to 100 %, data of $1/\rho_a$ larger than 10 $g^{-1}cm^3$ at w_f less than 20 % is omitted in the figure. Moreover, the samples with $1/\rho_a$ higher than 10 $g^{-1}cm^3$ were foams and they were different from samples reported in Figure 2. Experimental $1/\rho_a$ data are connected by a broken curve in the figure. Similar curves were obtained for other samples with different types of fillers. At filler contents larger than 40%, there is a linear relationship between w_f and $1/\rho_a$. The straight solid line connecting $1/\rho_f$ and the origin of the axes shows the filler volume. The estimated apparent filler density, ρ_{fe}, was recalculated in order to fit the experimental data.

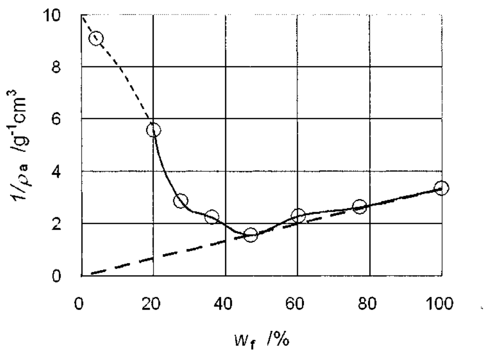


Figure 2. Relationship between reciprocal values of apparent density, 1/ ρ_a, and weight fraction, w_f of bamboo powder filled samples.

The schematic models of the fillers and polyurethane are shown in Figure 3. The axes of the graph are the same as those in Figure 2. The straight broken line shows the volume of fillers which was calculated using the weight fraction of fillers, w_f, and the filler, $1/\rho_f$. The model (f) in the figure shows the fillers without polyurethane. In this case, $1/\rho_a$ is equal to $1/\rho_f$. The model (d) and (e) show the samples, where all of the polyurethane can fill the space among fillers. The values of $1/\rho_a$ of these samples are on the straight line, since they show that the apparent volume of samples is equal to the apparent volume of fillers without polyurethane. The model (c) shows the samples which have a lower apparent density, $1/\rho_a$, than that of the fillers without polyurethane. In this model, the apparent volume of fillers is reduced and in addition all polyurethane can be placed into the space among the fillers. The model (b) shows the samples where some of the polyurethane is fills the space among fillers and the remaining part does not contain fillers. The latter part of polyurethane was not rigid but of the foam type. The model (a) represents the polyurethane without fillers. In this case, the polyurethane was also a foam type. The experimental data in the region where $1/\rho_a$ exceeded the minimum value almost agree with the straight line. Very likely the structures of these samples agree with the models (d) or (e). The experimental results in Figure 2 can be explained by using the structure models in Figure 3.

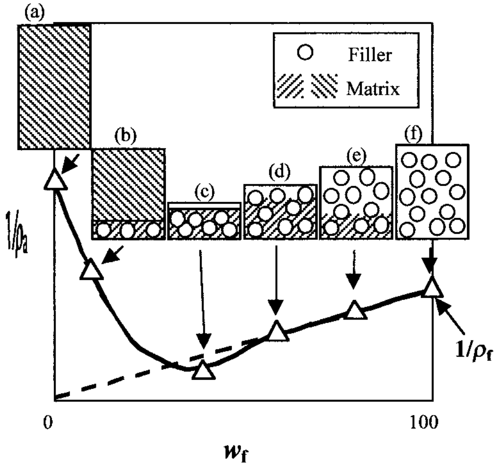


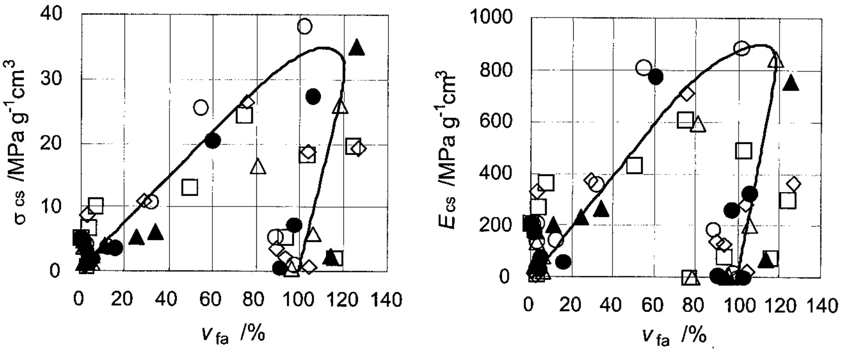
Figure 3. Schematic models of fillers and polyurethane matrix at various apparent density, $1/\rho_a$, and weight fraction, w_f; Δ: experimental data, broken line: apparent filler volume.

The average length along the principal axis, a_m, the aspect ratio, a_r, and the estimated apparent filler density, ρ_{fe}, are shown in Table 1.

Table 1. Average length, a_m, and aspect ratio, a_r and estimated apparent density, ρ_{fe}, of fillers.

Filler	a_m /μm	a_r	ρ_{fe} /g cm^{-3}
Bamboo powder	791	3.17	3.32
Roast bamboo powder	1203	3.74	3.16
Coffee grounds	1726	2.68	3.44
Ground coffee bean parchment	514	1.85	2.27
Wood meal	233	3.93	4.79
Cellulose	12	1.43	3.33

The effect of the filler content on the composite mechanical properties was related to the volume fraction of fillers, since the mechanical properties are strongly affected by this parameter. Accordingly, the apparent volume ratio of fillers, v_{fa} (%),which are expressed by the broken line in Figure 3, was calculated by equation (5) in the experimental section. In Figure 3, the v_{fa} values of the models (a) and (b) are lower than 100 %. that of the model (c) is greater than 100 %, and those of the models (d), (e) and (f) are equal to 100 %.



(a) (b)

Figure 4. (a) Relationship between the specific strength, σ_{cs}, and apparent volume ratio, v_{fa}, (b) Relationship between specific modulus, E_{cs}, and apparent volume ratio, v_{fa}; O bamboo powder, ● roast bamboo powder, ▲ coffee grounds, Δ ground coffee bean parchment, ◊ wood meal, □ cellulose.

The relationships between apparent volume ratio, v_{fa}, and the specific values of the mechanical properties of samples are shown in Figure 4. The figures (a) and (b) show the results of specific strength and specific modulus for compression tests, respectively. Master curves can be obtained for both relationships as shown in the figures. That is, regardless of the type of filler, both, σ_{cs} and E_{cs}, increase with increasing v_{fa} and reach the maximum at v_{fa}=100 %. Then σ_{cs} and E_{cs} decrease slightly, up to v_{fa}=120 %, and then linearly decay to decrease with zero at v_{fa}=100 %. Although f the experimental data show that some of v_{fa} values are greater than 100 %, the maximum of both σ_{cs} and E_{cs} is observed at around v_{fa}=100 %. This result indicates that the fillers affect more the mechanical properties of the samples with v_{fa}=100 % than those of samples with v_{fa} higher than 100 %. Figure 5, shows that the effect of the filler content on the composite mechanical properties can be evaluated from the apparent volume ratio regardless of the types of filler.

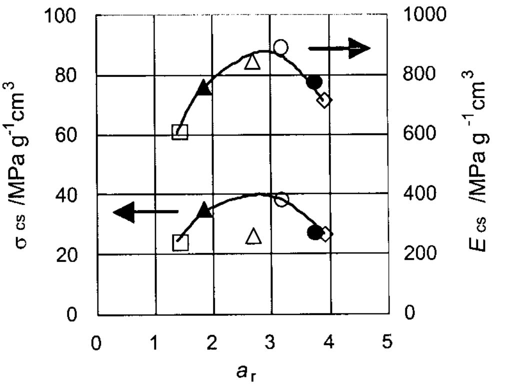


Figure 5. Relationship between the maximum values of mechanical properties, σ_{cs} and E_{cs}, and aspect ratio of fillers, a_r; O bamboo powder, ● roast bamboo powder, ▲ coffee grounds, Δ ground coffee bean parchment, ◊ wood meal, ☐ cellulose.

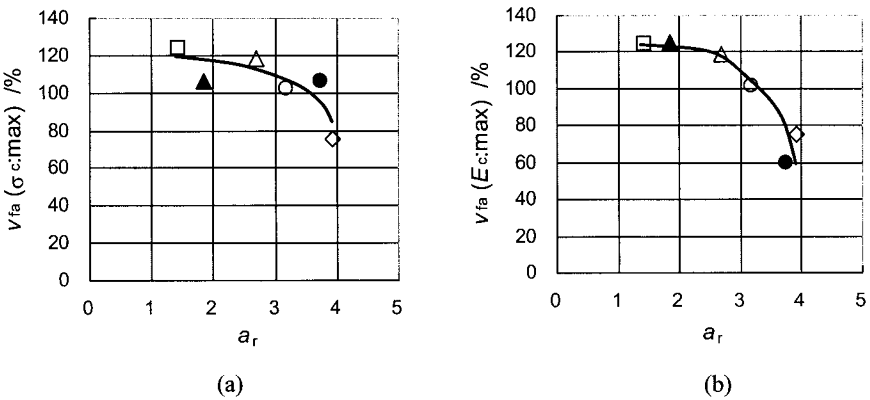


Figure 6. (a) Relationship between the apparent volume ratio, where the compression strength is maximized, and aspect ratio of fillers, a_r. (b) Relationship between the apparent volume ratio, where elastic modulus is maximized, and aspect ratio of fillers, a_r; O bamboo powder, ● roast bamboo powder, ▲ coffee grounds, Δ ground coffee bean parchment, ◊ wood meal, ☐ cellulose.

Characteristic values of v_{fa} that maximize σ_{cs} or E_{cs} are plotted against the aspect ratio of fillers, a_r, in Figure 6 (a) and (b). These values steadily decrease with increasing a_r. It is possible that the larger aspect ratio of fillers makes it more difficult for the polyurethane matrix to fill the space among the fillers. The maximum values of polyurethane composites filled with similar types of plant particles can be evaluated by the master curves shown in Figures 4, 5 and 6.

Conclusion

The effect of the filler shape on the mechanical properties of rigid type polyurethane composites was investigated, Molasses polyol and various kinds of plant particles, such as bamboo powder, roast bamboo powder, coffee grounds, ground coffee bean parchment, wood meal and cellulose were used as fillers. The effect of the filler content on the mechanical properties can be compared among the samples with different types of fillers, by evaluating the apparent volume of fillers without polyurethane as a standard value of volume. It was found that the curves that relate the specific mechanical properties and the apparent volume ratio is independent of the filler shape, such as mean length and aspect ratio. These curves indicate that the sample with bamboo powders having aspect ratio=3 shows the maximum values of mechanical properties. Finally it is shown that the maximum values of mechanical properties and the filler content can be evaluated from the aspect ratio and the apparent density of fillers.

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