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Fundamental Material Recycle of Unsaturated Polyester Resin

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As one first step of material recycling, reground unsaturated polyester resins were prepared with ground resins. Namely, cured unsaturated polyester resins were ground into powders and then sifted. Ground particles were mixed with virgin resins, and cured and postcured under the same conditions. We discussed the tensile properties of reground unsaturated polyester resins with different volume fractions and sizes of ground unsaturated polyester resin. The tensile strength lowered with increasing the size and the volume fraction of mixed particles. Taking the volume fraction and size of particles into consideration, the experimental equation was found to estimate the tensile strength of the recycling unsaturated polyester resin. The volume fraction-particle size superposition held for the tensile strength of reground unsaturated polyester resin.

Key words: Reground Unsaturated Polyester Resin, Tensile Strength, Cross-linking Density

1. INTRODUCTION

In the modern society, the exhaust problem of resources and the waste disposal are big substantial problems. In order to aim at an advanced use of resources, the technical developments of reuse and recycle are important. Recycling of thermosetting resins were generally difficult. As the recycling method of a waste plastic, the following methods are presented. ① Material recycling which waste is ground small and re-mixed, ②Chemical recycling which was prepared for chemical treatments, such as hydrolysis, methanol and glycolic decomposition, and conversed a monomer and chemicals, ③ Energy recycling which combustion heat is changed into energies, such as warm water, steam and electricity, and is reused.

In this study, material recycling of unsaturated polyester resin which is one of the representatives of thermosetting resin was discussed. First, the cured unsaturated polyester resins were crushed and ground in various sizes. Second, the ground resins were mixed into virgin resin by various volume fractions. We measured tensile properties of the materials produced in this manner.

2. EXPERIMENTAL

Unsaturated polyester resin used in this study was a Rigolac 2004WM-2 (Showa Koubunshi CO., Ltd). Curing agent was a Permek N (Nihon-Yushi Co., Ltd). First, the 100 parts unsaturated polyester resin and 1.5 parts curing agent were mixed. This mixture was agitated thoroughly and then defoamed. Then, it was poured into a mould and subjected to curing at 60℃ for 17h and to postcuring at 140℃ for 1h. It was naturally allowed to cool to room temperature. Second, the cured resins were reground by the ultracentrifugal grinder and screened by the solenoid-actuated shaking apparatus. Average size of particle obtained in this manner is shown in Table 1. Finally, virgin unsaturated polyester resin was mixed with ground resin and subjected to curing at 60℃ for 17h and to postcuring at 140℃ for 1h. Particle of ground unsaturated polyester resins were weighed with a volume fraction shown in Table 1.

Table 1 Volume fraction of particle.

Particle size(mm)	0.165	0.264	0.365	0.465	0.948
Volume fraction(%)	2.5, 5, 10, 20, 30				

3. RESULTS AND DISCUSSION

The relation between volume fraction of mixed particle and tensile strength is shown in Fig.1. The tensile strength lowered with increasing the volume fraction of mixed ground particle and with increasing the particle size. It is considered that the defect increases as volume fraction and particle size increase, and it becomes easy to generate stress concentration.

Nielsen[1)] has reported that the tensile strength of particle filled composites is dependent on the 1/3 power of the volume fraction of filler or 2/3 power, in case of a good bonding at the filler-matrix interface or a poor bonding, respectively. Namely, the tensile strength σ_c is given by the following equations, respectively:

$$\sigma_c = (1 - \phi_f^{1/3})\,\sigma_m \qquad (1)$$

$$\sigma_c = (1 - \phi_f^{2/3})\,\sigma_m \qquad (2)$$

where σ_m is the tensile strength of matrix, ϕ_f is the volume fraction of filler.

As seen in Fig.1, the calculated values by both Equations(1) and (2) are lower than the experimental values in the same manner as the results of epoxy resin[2]. It is considered that mixed ground particles prevent from cross-linking of resin at the time of the curing reaction of resin, and eventually reduce tensile strength.

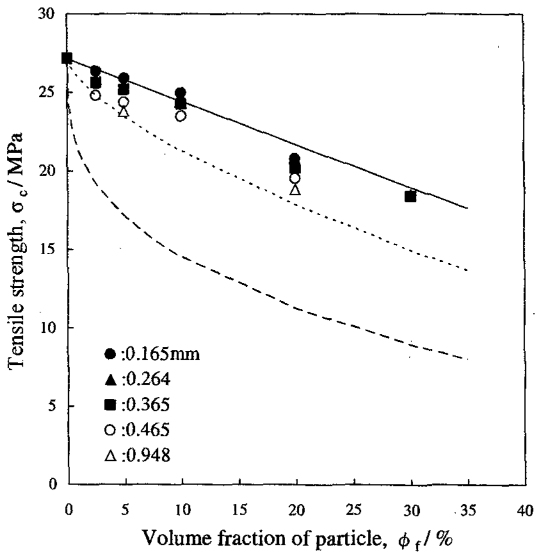

Fig.1. Relation between tensile strength and volume fraction of particle. ---- :Value calculated with eq.(1), ------ :value calculated with eq.(2), —— :value calculated with eq.(4)

We examined the effect of cross-linking density on the tensile strength. The relationship between tensile strength and cross-linking density is shown in Fig.2. Tensile strength decreases linearly as cross-linking density decreases in the same manner as the results of the epoxy resin[2]. The tensile strength σ at any cross-linking density ρ is given by the following equation:

$$\sigma = \sigma_0 \rho / \rho_0 \qquad (3)$$

where σ_0 and ρ_0 are the tensile strength and the cross-linking density of virgin resin, respectively.

We finally found that the effect of cross-linking density on the tensile strength is estimated by the following equation[2]:

$$\sigma_c = (1 - \phi_f)\,\sigma_m \qquad (4)$$

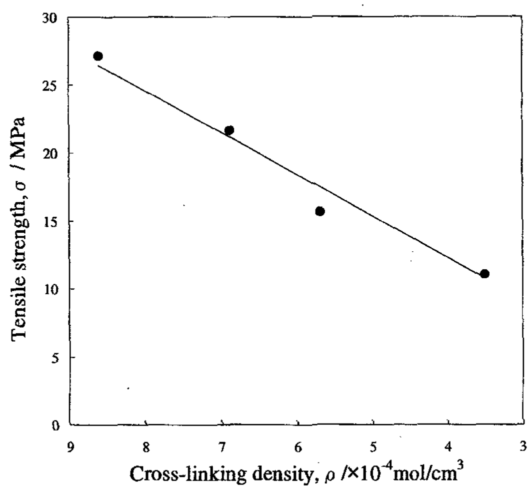

Fig.2. Relation between cross-linking density and tensile strength. —— :Value calculated with eq.(3).

where σ_c and σ_m are the tensile strength of reground and virgin unsaturated polyester resin, respectively, and ϕ_f is the volume fraction of ground particle.

The solid line in Fig.1 shows values calculated by the Equation(4). Calculated values are almost the same as the experimental values of unsaturated polyester resin mixed ground particle with the smallest size. But, all experimental values can't be estimated by the Equation (4).

We next discussed the effect of particle size. The relationship between the $d^{-1/2}$, d is particle size, and the relative tensile strength σ_c/σ_m is shown in Fig.3. The relative tensile strength σ_c/σ_m increases linearly with the $d^{-1/2}$ [3], and the slope is almost the same.

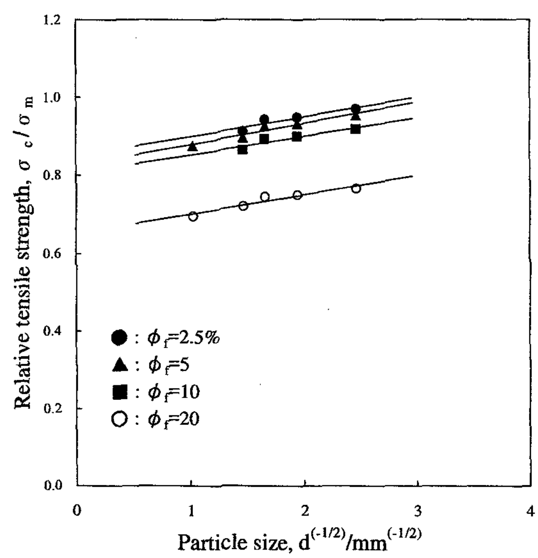

Fig.3. Relation between $d^{(-1/2)}$ and tensile strength.

Therefore, the effect of the ground particle size on the tensile strength of mixed resin is represented by the following equation:

$$\sigma_c/\sigma_m = b_s + k_s d^{-1/2} \qquad (5)$$

where σ_m and σ_c are the tensile strength of virgin and reground unsaturated polyester resin, respectively, d is the ground size of mixed particle, and k_s and bs are constants. The solid lines in Fig.3 are values calculated from the Equation (5).

The relationship between the volume fraction of particle and constant b_s obtained from Fig.3 is shown in

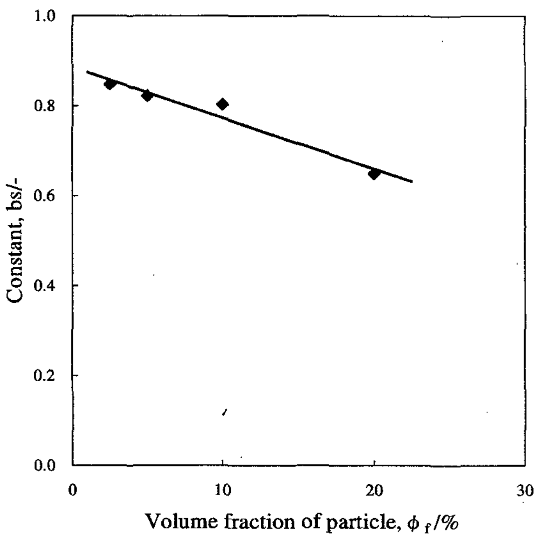

Fig.4. Relation between volume fraction of particle and constant b_s. ——— : Value calculate with eq.(6).

Fig.4. The constant b_s decreases almost linearly with the volume fraction of particle. b_s is therefore given by the following equation:

$$b_s = b_{s1} + b_{s2}\,\phi_f \qquad (6)$$

where b_{s1} and b_{s2} are constants. The solid line in Fig.4 is value calculated by the Equation (6).

Accordingly, the tensile strength of recycled unsaturated polyester resin mixed ground particles is given by the following equation obtained by substituting the Equation (6) into the Equation (5):

$$\sigma_c = \sigma_m[(b_{s1} + b_{s2}\,\phi_f) + k_s d^{-1/2}] \qquad (7)$$

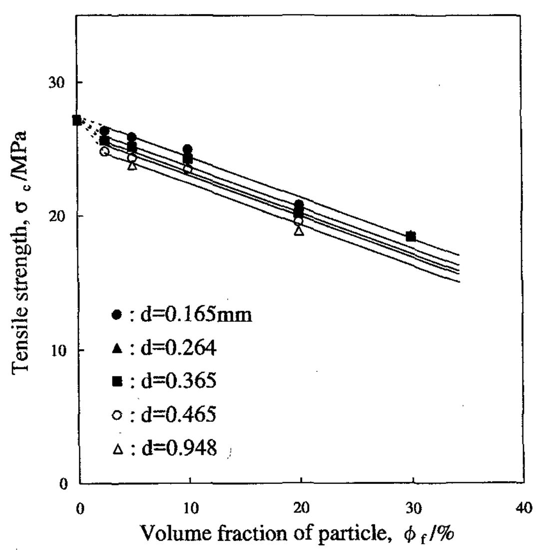

Fig.5. Relation between volume fraction of particle and tensile strength. ——— :Value calculated with eq. (7).

The solid lines in Fig.5 are the values calculated from the Equation (7). In this experiment, the constant b_{s1} is 0.88, the constant b_{s2} is -1.12 and the constant k_s is 0.05. The calculated values were almost the same as the experimental results. Accordingly, the tensile strength of reground unsaturated resin may be estimated by the Equation (7).

As reported in previous paper[2], the tensile strength of recycled epoxy resin mixed ground particle was also estimated by the Equation (7). It is therefore considered the Equation (7) is valid for the tensile strength of recycled resin with ground particle.

Data in Fig.5 have been shifted along the volume fraction axis to obtain master curve of the tensile strength, as shown in Fig.6. In this figure, the reference particle size is 0.165mm, which is the smallest size in this experiment. Although there exists a slight deviation, it is possible to reduce the data to a single master curve. This implies that the volume fraction of particle-ground particle size superposition holds for the tensile strength of reground unsaturated polyester resin.

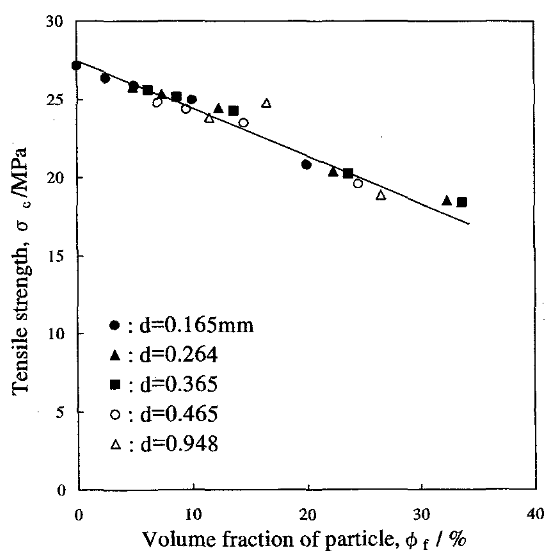

Fig.6. Tensile strength master curve (reference particle size is 0.165mm). ——— :Value calculated with eq.(7).

The solid line in Fig.6 is value calculated by the Equation (7). The calculated values are almost the same as the experimental values.

Fig.7 shows the shifted volume fraction of mixed particle to obtain master curve. The shifted volume fraction increases with particle size.

From the Equation (7), the shifted volume fraction $\Delta\phi_f$ of mixed particle can be obtained by the following equation:

$$\Delta \phi_f = k_s(d_a^{(-1/2)} - d_s^{(-1/2)})/b_{s2} \quad (8)$$

where d_s is the reference particle size, d_a is the desired particle size. The shifted volume fractions of mixed particle shown in Fig.7 are values calculated from the Equation (8).

In this experiment, it is considered the master curve of the tensile strength may be estimated by the Equations (7) and (8).

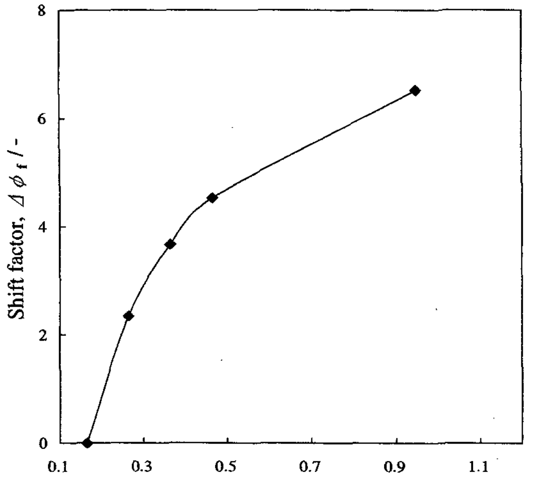

Fig.7. Shifted volume of fraction as a function of particle size. ——— :Value calculated with eq.(8).

Young's modulus of reground unsaturated polyester resin is shown in Fig.8. Regardless of the volume fraction and size of particle, Young's modulus is almost unchanged and is almost equal to the one of virgin unsaturated polyester resin. This tendency is the same as that of epoxy resin[2].

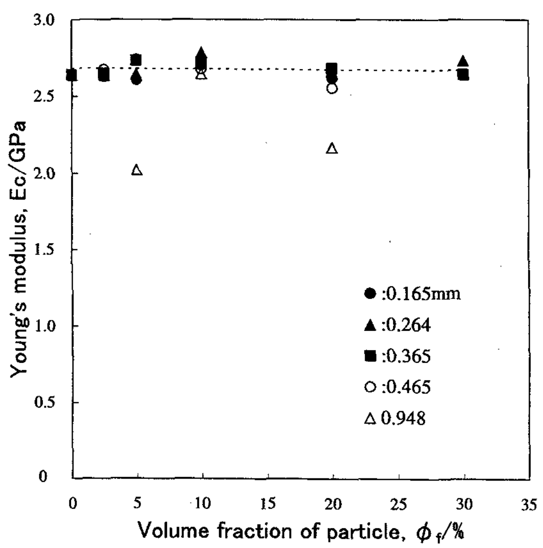

Fig.8. Relation between volume fraction of particle and Yong's modulus.

Tensile breaking strain of reground unsaturated polyester resin is shown in Fig.9. The tensile breaking strain lowered with increasing the volume fraction of mixed ground particle and with increasing the particle size, in the same manner as epoxy resin[2].

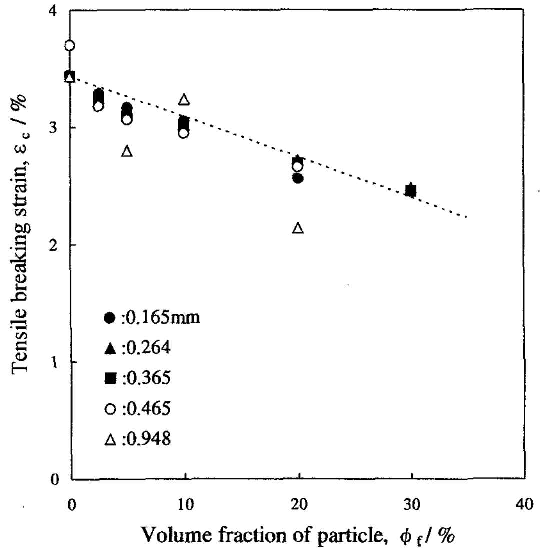

Fig.9. Relative between volume fraction of particle and tensile breaking strain.

4. CONCLUSIONS

Unsaturated polyester resins were ground into powders and then sifted. Ground particles were mixed with virgin resins, and cured and postcured under the same conditions as the curing ones of virgin resins. The tensile properties of reground unsaturated polyester resins with different volume fractions and sizes of ground unsaturated polyester resin were discussed. The tensile strength lowered with increasing the size and the volume fraction of mixed particles. Taking into both the volume fraction and size of particles consideration, the experimental equation was found to estimate the tensile strength of the recycling unsaturated polyester resin. The volume fraction-particle size superposition held for the tensile strength of reground unsaturated polyester resin.

Young's modulus was almost unchanged and was almost equal to the one of virgin unsaturated polyester resin. Tensile breaking strain was lowered with increasing the volume fraction and the particle size of mixed ground particle.

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