

Experimental and Theoretical Studies on Crumb Rubber/ Polyurethane Blend System

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Abstract: Recycling of waste materials is a field of great attention in all industries. Reclaiming, re-treading and using the energy by heating have been employed for recycling the waste tires. Recycling on the other hand involves incorporation of small particles obtained from the discarded tires. Rubber sheet using the waste tire grinded scrap which is called "crumb rubber" was prepared and investigated in this study. The effect of the size of the crumb rubber on the properties of the crumb/polyurethane blend was studied in parallel with the optimum binder content for good mechanical properties. Also this paper covered the effect of fillers on the mechanical properties of the blends. The deformation patterns of the crumb rubber/polyurethane sheet were predicted by finite element analysis. The predicted behaviors were consistent with experimental results. Therefore, this numerical works will be useful to effectively design elastomeric components.

Introduction

The recent explosive increase in the number of automobiles, has given rise to the problem of disposal of the waste tires. This by-product of industrialization seriously threatens the environment, thus urgent measures are highly needed.

In general, three methods of treatment of waste tires have been developed. The first is combustion. The second is burial under ground. These methods, however, lead to other environmental problems such as air pollution and water pollution. The third is recycling, which is acknowledged to be the best.^{1,2}

The oldest method of recycling waste tires is reclaiming.³ Retreading⁴ has also been employed for many years although it has recently become less common. Another strategy is to use the energy by heating. Both incineration and pyrolysis methods are available for large scale recycling. Powder utilization is commercially used method. Powdered or crumb rubber obtained from the used tires by grinding in ambient process or cryogenic process. The crumb rubber can be used in several ways. It can be applied to play

ground surfaces, running tracks, and rubber blocks, etc.⁵⁻⁹ Crumb rubber can be incorporated in roofing materials. Another potentially large volume application is for pavements.^{10,11} Crumb rubber modified asphalt improves road life, crack resistance and anti-skid properties. Although the powder utilization is easy to apply with simple equipment, difficulties arise in processing. This paper discusses rubber powder processing by studying the effects of size of crumb rubber, and the amounts of binder and filler.

For the prediction of deformation behavior of crumb rubber sheet under load, a numerical simulation was carried out and compared with experimental results.

Experimental

Materials. Three different sizes of scrap rubber particles were used in this study. The coarse medium and fine crumb rubbers were designated to "A", "F" and "C", respectively. The composition of the scrap rubber particles are summarized in Table I. Polyurethane(PU) was used as a binder. The composition and basic

Table I. Composition of Crumb Rubber Used in This Study

Composition		Content(phr)
Polymer Base(Natural Rubber)		100
Carbon		78.3
Additives	Total	26.6
	Oil	18.4
	Sulfur	3.6
	Accelerator	2.1
	Antidegradant	1.8
	Stearic Acid	0.7
Wax		0.6
ASH		6.1

properties of PU are summarized in Table II and Table III. Two size of stone powders and glass fiber were used for investigation of the effect of fillers on the properties of the blends.

Sample Preparation. Sample was prepared by mixing, curing/shaping, and cutting. As the first step for sample preparation, crumb rubbers were mixed with polyurethane binder by agitation at room temperature. The second step involves compression molding of the mixture at 150 °C for 10 min by using a hot press. During this procedure, the sample was cured and shaped. The cured rubber sheet was cut into stand-

Table II. Composition of Polyurethane Binder Used in This Study

Composition	Weight Percentage
Diphenyl methane-4,4'-diisocyanate	25-28
Polybutadiene	45-55
Polyether	15-20
Plasticizer	10-15
Additives	2-4
Total	100

Table III. Properties of Polyurethane Binder Used in This Study

Test	Hardness	Tensile Strength (kg/cm ²)	Elongation (%)	Specific gravity
Before aging	78	41	110	1.020
After aging (100 °C, 24 hr)	80	54	120	1.020

ard specimens.

Test Methods. The size of the crumb rubber was measured by a particle size analyzer. The tensile strength and elongation at break of the samples using an Instron universal tensile tester with a cross-head speed of 300 mm/min at room temperature, according to KSM(Korean Standard Method) 6518.¹² Heat aging of the rubber samples was carried out in an oven maintained 100 °C for 24 hr. A press was used to observe the deformation behavior of rubber sheet.

Theoretical

Numerical Analysis. Although many research works have been done by numerical analysis in the field of polymer processing, the studies on elastomer fields are relatively few due to the nonlinear stress-strain relationships, caused by the large deformation of the material. More than all elastomers have incompressible characteristics and time dependent behavior under the applied force.¹³ In spite of such difficulties, the unique features of elastomers forced engineers in rubber industry to solve the problems. As a result, many theoretical models have been developed and Finite Element Analysis(FEA) on the elastomers has been studied since 1960s.¹⁴⁻¹⁶ However insufficient information, inexact model, and boundary conditions lead to inadequate solution in FEA. In this study, to predict the deformation behavior of the rubber samples under an applied force, a finite element analysis was applied as follows:

The equilibrium equation which may be expressed by

$$\sigma_{ij,j} = 0 \quad (1)$$

Here σ is the total stress tensor and comma (.) means the differentiation.

The constitutive equation are expressed by,

$$\sigma_{ij} = \tau_{ij} - P \delta_{ij} \quad (2)$$

$$\tau_{ij} = 2\mu(\epsilon) \Delta \epsilon'_{ij} \quad (3)$$

where τ_{ij} is deviatoric stress tensor, P an hydrostatic pressure, δ_{ij} Kronecker delta, μ an elastic coefficient, and $\Delta \epsilon'_{ij}$ a deviatoric strain in-

crement during small time Δt .

The strain increment function is defined as

$$\Delta \epsilon'_{ij} = \frac{1}{2} (\Delta u_{i,j} + \Delta u_{j,i}) \quad (4)$$

where Δu represents a deformation tensor.

Now, we considered how to obtain the elastic coefficient. The stress and strain are defined as

$$\bar{\sigma} = \sqrt{(3/2) \tau_{ij} \tau_{ij}} \quad (5)$$

$$\bar{\epsilon} = \sqrt{(2/3) \Delta \epsilon'_{ij} \Delta \epsilon'_{ij}} \quad (6)$$

Equations (5) and (6) are substituted into Eq.(3), then $\bar{\mu}$ is

$$\bar{\mu}(\epsilon) = \frac{1}{3} \frac{\bar{\sigma}}{\bar{\epsilon}} \quad (7)$$

The rubber may be considered as an incompressible material, then

$$\Delta u_{i,i} = 0 \quad (8)$$

For calculation, we used the following boundary conditions :

$$\sigma_n = -\beta(\Delta u_n - \Delta \bar{u}_n) \text{ on } \Gamma_c \quad (9)$$

$$\sigma_t = -\mu \sigma_n \text{sign}(\Delta u_t - \Delta \bar{u}_t) \text{ on } \Gamma_c \quad (10)$$

$$\sigma_{ij} n_j = 0 \text{ on } \Gamma_f \quad (11)$$

where subscripts n and t represent normal and tangential, respectively. Γ_c and Γ_f represent the boundaries of contact surface and free surface, respectively. Here, \bar{u} is defined as a multiplying velocity, \bar{u} , with time increase, t . We used the values of $\bar{u} = -1$ and $\beta = 1,000,000$ in program.

Since we assume that the frictionless on the boundary, the weak form is expressed as

$$\int_{\Omega} \tau_{ij} \omega_{i,j} \Omega - \int_{\Omega} P \omega_n d\Omega - \int_{\Omega} u_{i,i} q d\Omega - \int_{\Gamma_c} -\beta(\Delta u_n - \Delta \bar{u}_n) \omega_n d\Gamma = 0 \quad (12)$$

where ω and q are weighting function and ω_n is defined as

$$\omega_{ij} = (\omega_{i,j} + \omega_{j,i})/2 \quad (13)$$

Prediction of Deformation Behavior. Introduction of computer brought human being to revolutionize in the modern industry. With development of simulation techniques, it has become an essential factor in the areas of desining, planning and process controlling. The rheo-

logical properties of the crumb rubber/PU blend should be provided to predict the deformation behavior of the blend numerically. The relationship between the deformation and stress is obtained from the stress-strain curve of experimental data. From the Figure 1, the Mooney-Rivlin¹⁶ equation is used in this study.

$$\bar{\sigma} = 2[C_1(\bar{\lambda} - \frac{1}{\bar{\lambda}^2}) + C_2(\bar{\lambda} - \frac{1}{\bar{\lambda}^3})] \quad (14)$$

where λ is the stretch ratio, $1 + \bar{\epsilon}$. The values of constant $C_1 = 1.7543 \times 10$, and $C_2 = -1.7984 \times 10$ are obtained from experimental data. Figure 1 shows the stress-strain curve comparing experimental to theoretical data. Using these data and equations, the deformation patterns of rubber sheet according to applied force were compared theoretically with experimental as shown in Figure 2. The theoretical results were well consistent with experimental results. Therefore, the author believes that this numerical work will be useful for the design of crumb rubber sheet.

Results and Discussion

Effect of Binder Contents. The mechanical properties with different weight fractions of polymer binder to the crumb rubber were studied. Also the aging effect of the materials was investigated.

Figure 3-a indicates that the maximum value

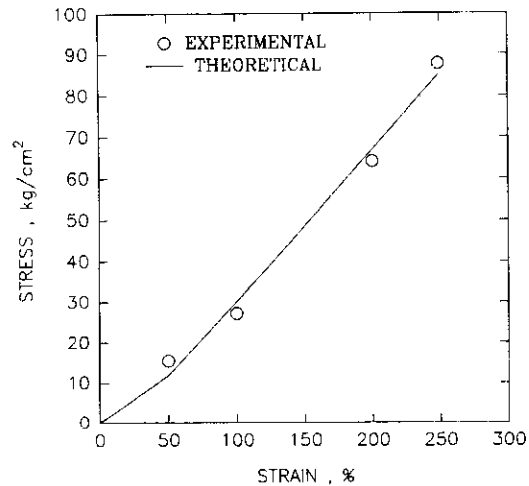


Figure 1. Stress-strain curve of crumb rubber/PU blend.

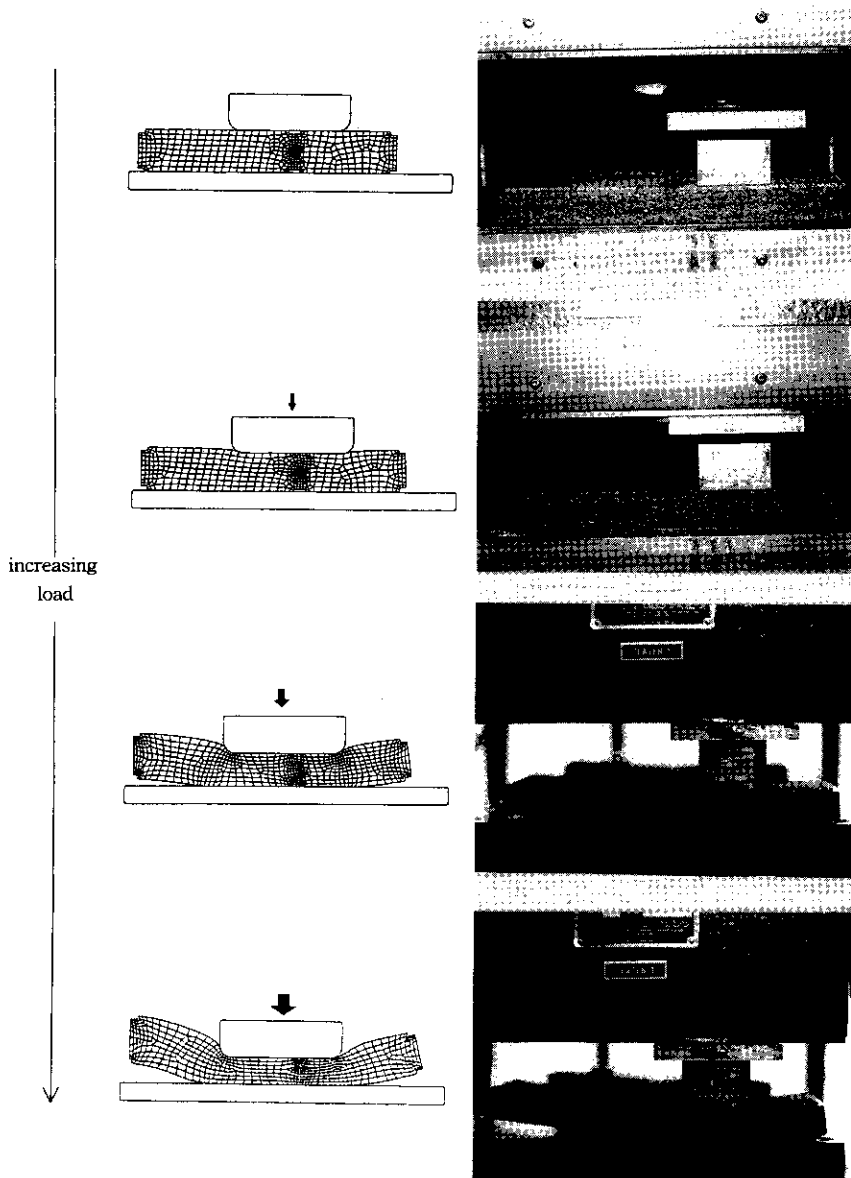


Figure 2. Deformation pattern of crumb rubber/PU blend sheet.

of the tensile strength was shown at 15phr of binder for using the crumb rubber "F". The effect of the aging, however, was not observed in this experiment. The values of elongation to break showed similar behavior to those of tensile strength (see Figure 3-b). These results indicated that insufficient amount of the polymer binder led to a poor coverage between polymer binder and crumb rubber, which results in de-

creased tensile properties. On the other hand, excess amount of polymer binder also induced to a poor tensile strength and elongation. One possible reason for this is the chain restriction. When an elastomer is deformed by an external force, part of the input energy is stored elastically in the chains and is available as a driving force for fracture. The remainder of the energy is dissipated through molecular motions into

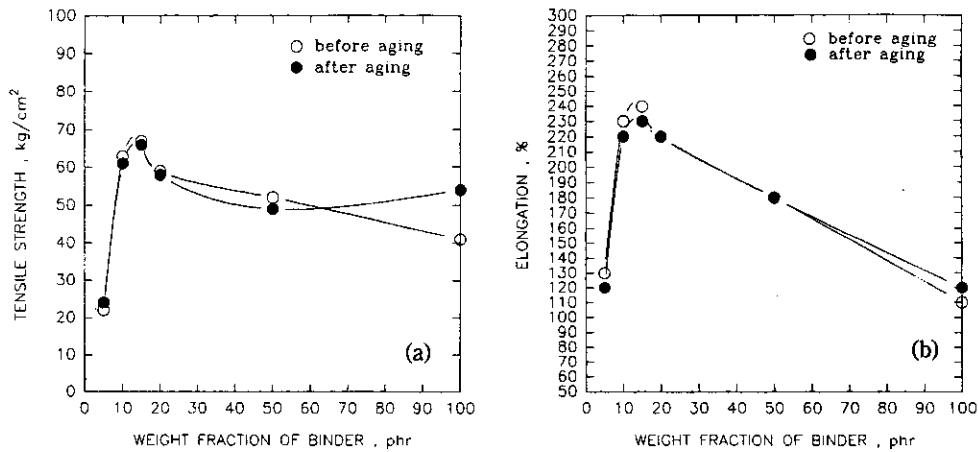


Figure 3. (a) Effect of fillers on tensile strength and (b) effect of fillers on elongation at break.

heat and is became unavailable to break the chain. At high level of binder, the chain motion become restricted and the network is incapable of dissipating much energy. The results relatively easily showed a low tensile strength and a low elongation.

Effect of Size of Crumb Rubber. Three different sizes of the crumb rubber were used, which are summarized in Table IV. The crumb, C, and the medium size of crumb. F were mixed. Also the coarse crumb rubber, A, and medium size of crumb were mixed to compare the size effect.

Figure 4-a shows the tensile strength versus

Table IV. Characteristics of Three Kinds of Crumb Rubbers Used in This Study

Sample	Size(mm)	Heat Loss(%)	Volatile(%)
A	2.8~3.9	0.76	64.04
F	0.7~2.5	0.51	67.17
C	10 ⁻² ~10 ⁻¹	2.03	61.29

weight fraction of coarse and fine crumb rubber to the medium one. These samples comprised 100 parts of crumb rubber and 10 parts of polyurethane binder. Both of coarse rubber blend and fine rubber blend to the medium size crumb rubber showed a lower value of tensile strength. The

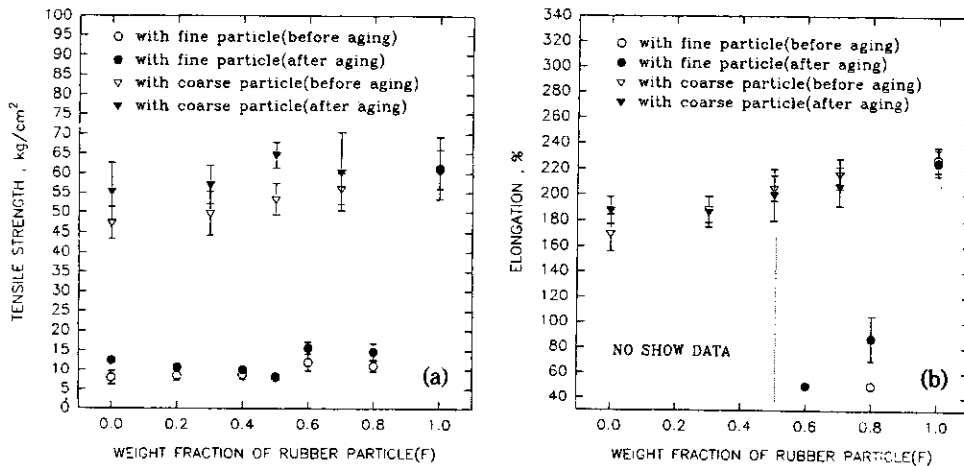


Figure 4. (a) Effect of size of crumb rubber on tensile strength and (b) effect of size of crumb rubber on elongation at break.

system of fine crumb rubber showed a very lower value of the tensile strength than that of the coarse size of rubber blend system. The elongation tendency was very similar to that of the tensile strength, which is shown in Figure 4-b. Especially, when adding more than 50% of the fine crumb rubber into the medium crumb, it was easily broken. However, the aging effect did not observed in this experiment.

These results indicated that the fine crumb rubber induced a poor adhesive coverage because it had a large surface area for wetting and increased interparticle spacing which results in a lower properties. The coarse crumb rubber showed a poor wetting. The reason may be explained by the occurrence of void region with a big size of crumb in the blend which led to crack at a lower break point. Therefore, the optimum size of the crumb rubber relates to the appropriate adhesion. The size distribution of rubber F, which showed the best properties is shown in Figure 5. The range of rubber particle size for the best results in this blending system was from 0.7 mm to 2.5 mm.

Effect of Fillers. Elastomers are often filled with particulate materials to obtain a desirable mechanical properties or cost reduction. The effect of fillers is highly dependent on their shapes, size, and quality of the filler/matrix interface.

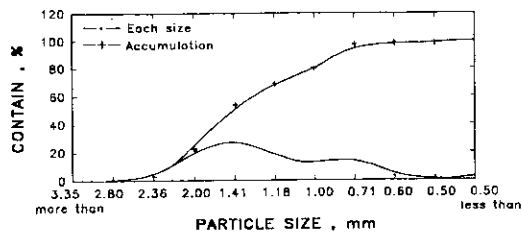


Figure 5. Particle size distribution curve of scrap rubber F.

Two different sizes of stone powders and a glass fiber were used as the filler in this experiment. We mixed 100 parts of the medium size crumb rubber and 10 parts of polyurethane with fillers to prepare the samples. Figure 6 shows the effect of the filler on the tensile properties of the blend. The tensile strength of the crumb/PU blend with the smaller size stone powder were lower than that of the blend with the larger size stone powder. The tendency of behavior decreased with increasing content of stones powders in the blends. When mixed with glass fiber, the tensile strength increased slightly with increasing the amount of the glass fiber (Figure 6-a). The elongation at break decreased with increasing of content of all these fillers (Figure 6-b).

These results indicated that the fillers acted as an inhibitor for the adhesion between crumb

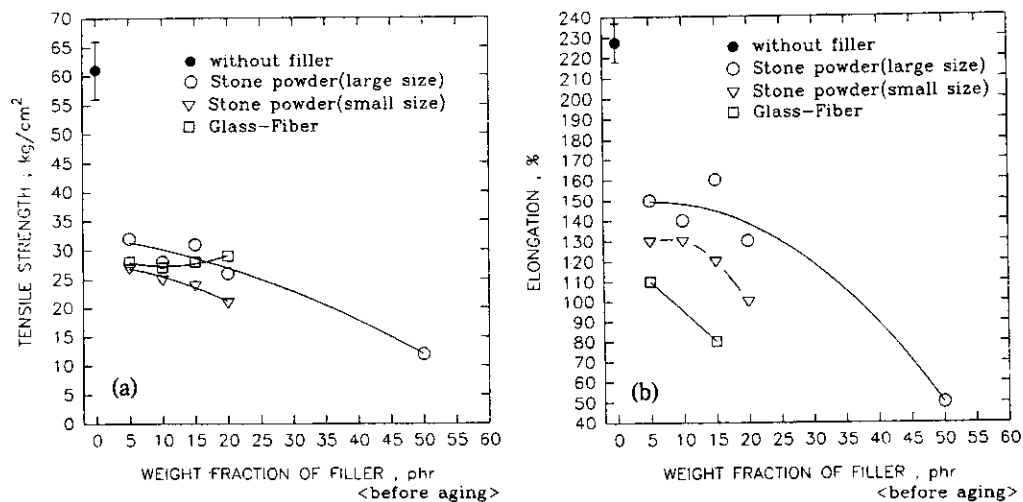


Figure 6. (a) Effect of fillers on tensile strength and (b) effect of fillers on elongation at break.

rubber and PU binder in this blending system. Insufficient adhesion leads to a reduced level of stress transfer for yielding across the interface between the rubber and polymer binder; thus, results in a lower tensile strength and elongation. To recognize these behavior, optical micrographs of each systems are shown in Figure 7.

In case of the blend filled with stone powder, the smaller stone powder induced the more debonding points in the blend which led to insufficient adhesion. The results showed that both the stone powder and the glass fiber act as a debonder in this blending system. However, the tendency of the tensile strength of the filled with glass fiber showed different from that of the filled with stone powder according to the loading amount. It may be explained by the fact that glass fiber having a long aspect ratio contributed to the reinforcing of the elastomers as well as weakening of the filler/matrix interface.

Conclusions

This research studied with a typical crumb rubber which was obtained from used tires in order to recycle them. The following conclusions are obtained from this study.

1. The size of crumb rubber must be considered as an important variable for a good quality of recycled products. Both the fine and coarse crumb rubber showed a poorer prop-

erties than that of the crumb which range of size is 0.7 - 2.5 mm.

2. The best adhesion between crumb rubber and polyurethane binder was showed at 15phr of binder content.

3. The fillers decreased adhesive force of the polymer binder in the crumb rubber/PU blend system. Sometimes they are, however, necessary to reduce the cost of products in the view of commercial side.

4. The predicted deformation behaviors of crumb rubber/PU blend by using FEA(finite element analysis) well agreed with experimental results.

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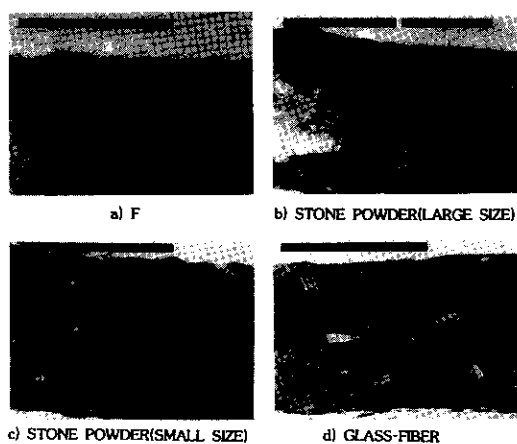


Figure 7. Optical micrographs of rubber samples($\times 50$).