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## Ultrasonic Degradation and Block Copolymerization of Polybutadiene with Acrylic Acid

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## ULTRASONIC DEGRADATION AND BLOCK COPOLYMERIZATION OF POLYBUTADIENE WITH ACRYLIC ACID

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### ABSTRACT

The ultrasonic degradation of polybutadiene (PB) and block copolymerization of PB with acrylic acid (AA) in cyclohexane solution were studied. The results show that the chain-scission reaction of PB follows the equation  $\overline{M}_t = (\overline{M}_0 - \overline{M}_\infty)e^{-kt} + \overline{M}_\infty$ , where  $k = 33.33 \times 10^{-5} \text{ s}^{-1}$ . The structure of the copolymer was identified by IR and NMR, and is a block one. The mechanism of the coupling effect of the copolymer (PB-*b*-AA) prepared in the CaCO<sub>3</sub>/SBR system was also studied by means of SEM and IR. The surface properties of CaCO<sub>3</sub> treated with the copolymer and the morphology of the fracture surface of vulcanized SBR/CaCO<sub>3</sub> were examined. The compatibility and mechanical properties of the SBR/CaCO<sub>3</sub> system greatly improved.

### INTRODUCTION

Polymer-polymer compatibility is a subject of considerable interest in polymer science. The question of finding an effective compatibilizer to improve the compatibility of an incompatible system is the key to preparing a new multicomponent material with polyfunctionality. The compatibility of a polymer blend may be enhanced by a block or graft copolymer having segments of similar structure or solubility parameters as the polymer-polymer or polymer-filler being mixed. In this paper the ultrasonic degradation of polybutadiene (PB) and its copolymerization in cyclohexane solution are studied. PB is compatible with most vinyl and diene polymers, while polyacrylic acid (PAA) is compatible with certain inorganic fillers.

Thus, PB-*b*-AA is expected to be an effective coupling agent for filled vinyl or diene polymers. The mechanism of the coupling effect of (PB-*b*-AA) in the SBR/CaCO<sub>3</sub> system is studied.

## EXPERIMENTAL

### Materials

*PB*: cis-content 96%,  $M_n = 6.77 \times 10^5$ .

*AA*: Purify commercial AA by distillation under vacuum at 60°C.

*Butadiene-styrene rubber*: SBR-1500, commercial quality.

*CaCO<sub>3</sub> (light)*: particle size 3–7 μm.

### Ultrasonic Reactor

The reactor is the same as reported in References 1 and 2. The wave frequency is 21.5 kHz, and the conical amplitude probe is 250 mm long with an end diameter of 20 mm.

### Ultrasonic Degradation of PB

Hydroquinone (free radical terminator) was added to PB in its cyclohexane solution. The degradation reaction was then carried out under different conditions.

### Ultrasonic Copolymerization of PB with AA

A 2% cyclohexane solution of PB containing a certain amount of AA was irradiated for a certain period at a given temperature with a sonic intensity corresponding to 370 W. The copolymer formed was then isolated according to the scheme shown in Fig. 1.

### Analysis and Identification

The structure of the copolymer was determined by IR and NMR. The coupling effect of the copolymer prepared in the SBR/CaCO<sub>3</sub> system was examined by SEM and IR.

## RESULT AND DISCUSSION

### Ultrasonic Degradation of PB

Figures 2–4 show that molecular weight of PB decreases very rapidly in the early stage of irradiation and gradually trends toward a limiting value ( $\bar{M}_\infty$ ) with time. The degradation increases with increasing sonic intensity but with decreasing solution concentration and temperature.

Baramboim suggested the following equation for polymer degradation under stress:

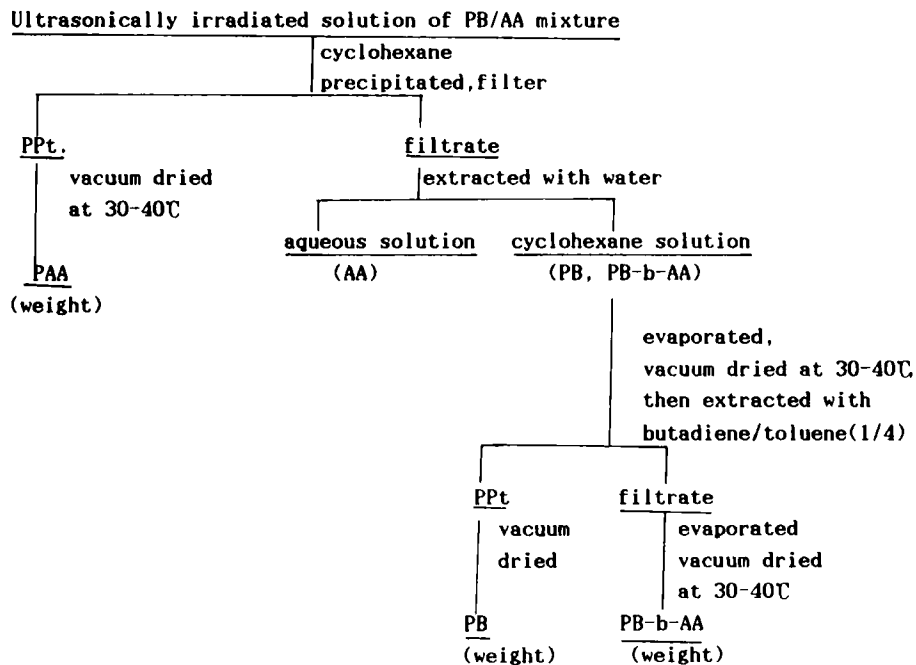


FIG. 1. Separation scheme of PAA, PB, and PB-b-AA copolymer.

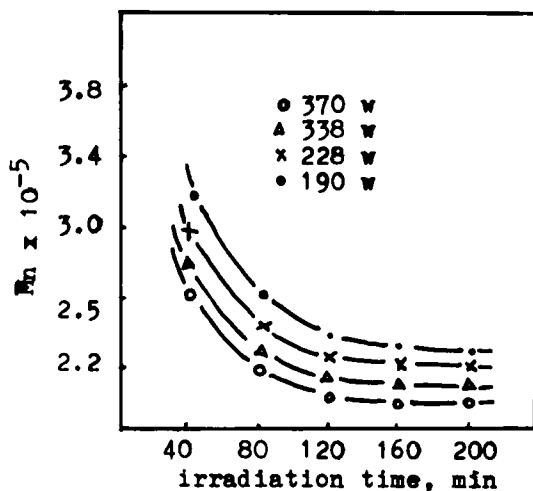


FIG. 2. Ultrasonic degradation of PB at different sonic intensities (2% PB, 20°C).

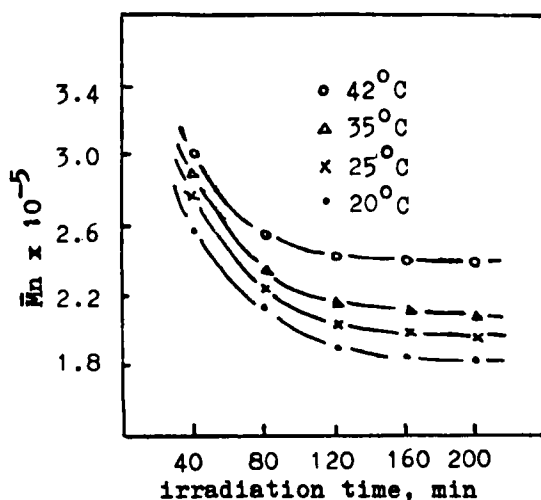


FIG. 3. Ultrasonic degradation of PB at different temperatures (2% PB, 370 W).

$$\bar{M}_t = (\bar{M}_0 - \bar{M}_\infty)e^{-kt} + \bar{M}_\infty \quad \text{or} \quad \ln(\bar{M}_t - \bar{M}_\infty / \bar{M}_0 - \bar{M}_\infty) = -kt$$

where  $M_t$  and  $M_\infty$  are the viscosity-average molecular weight of the sample at irradiation time  $t$  and its limiting value, respectively; and  $k$  is the reaction velocity constant. As shown in Fig. 5, the kinetic curve fits the experimental data very well;  $k$  (slope of the straight line, Fig. 5) equals  $33.33 \times 10^{-5} \text{ s}^{-1}$ .

#### Ultrasonic Copolymerization of PB and AA

As shown in Figs. 6 and 7, the yield of copolymer [(copolymer weight/PB added)  $\times 100\%$ ] increases with an increasing amount of AA added and decreasing reaction temperature. The yield decreases immediately after the maximum is

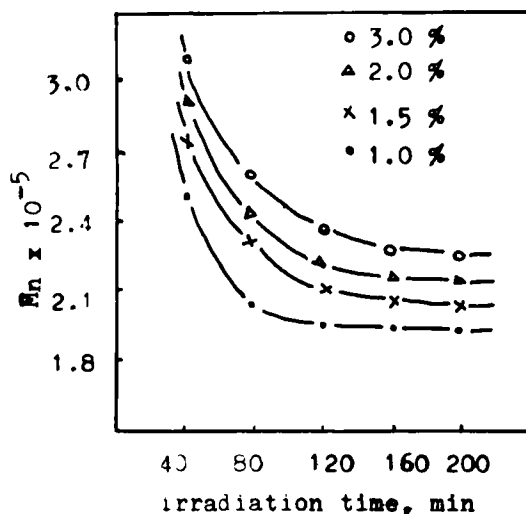


FIG. 4. Ultrasonic degradation of PB at different concentrations (370 W, 35°C).

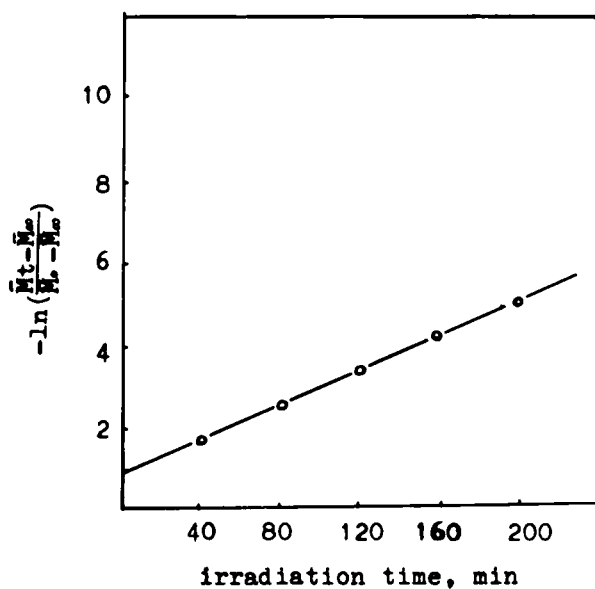


FIG. 5. Dependence of  $\ln\left(\frac{\bar{M}_t - \bar{M}_\infty}{\bar{M}_0 - \bar{M}_\infty}\right)$  on irradiation time (370 W, 2%, 35°C).

reached owing to a diminishing amount of AA present in the reaction system and due to chain scission of the copolymer formed.

The AA content in the copolymer increases with an increase in the amount of AA added to the reaction system, and reaches a maximum at 120 min (Fig. 8). As compared with the IR spectrum of PB, the IR spectrum of the copolymer (Fig. 9) exhibits some new absorption peaks at 3200–3400, 1728, and 2338–2624  $\text{cm}^{-1}$  due to the presence of  $-\text{COOH}$  and anhydride groups. In the NMR spectrum of the

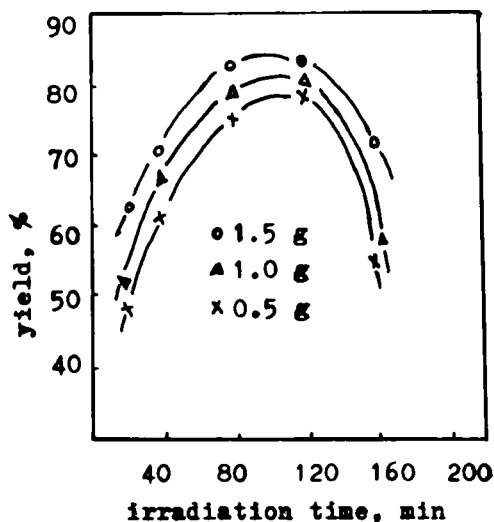


FIG. 6. Dependence of copolymer yield on amount of AA added (370 W, 2%, 35°C).

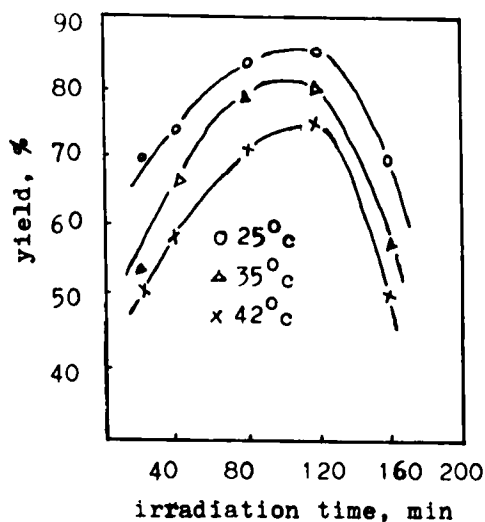


FIG. 7. Dependence of copolymer yield on reaction temperature (370 W, 2%, 1.0 g AA).

copolymer (Fig. 10), the chemical shifts at 0.8977–0.9489 and 1.194–1.3736 are due to shifts of CH and CH<sub>2</sub>, respectively, in

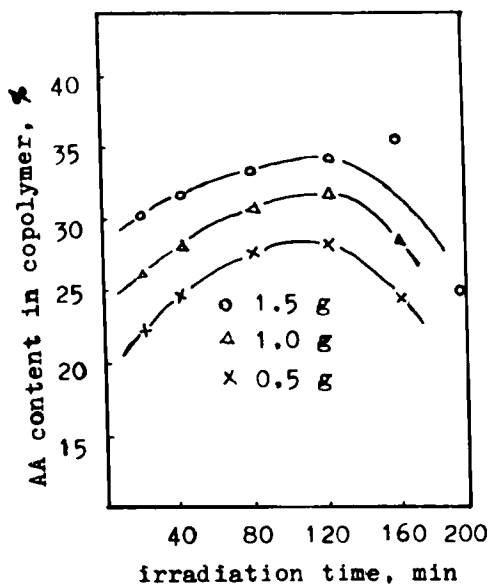
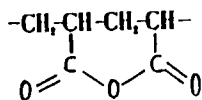


FIG. 8. Dependence of AA content in copolymer on amount of AA added (370 W, 2%, 35°C).

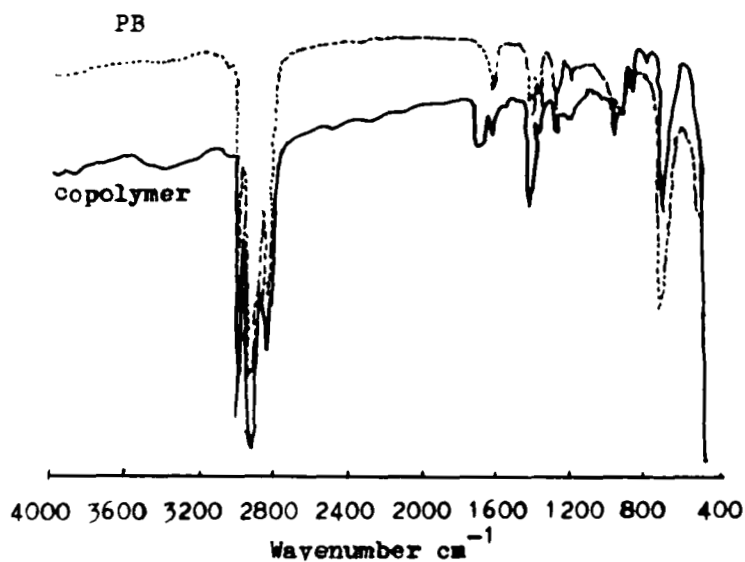


FIG. 9. The IR spectra of PB and PB-*b*-AA copolymer.

excluding the possibility of grafting AA at these positions. Thus, the copolymer may be considered to be a block one.

#### Coupling Effect of PB-*b*-AA Copolymer in SBR/ $\text{CaCO}_3$ System

Figure 11 is the IR spectrum of  $\text{CaCO}_3$  treated with the PB-*b*-AA copolymer. The characteristic absorption peak of the copolymer at 2857-3072  $\text{cm}^{-1}$  remains in

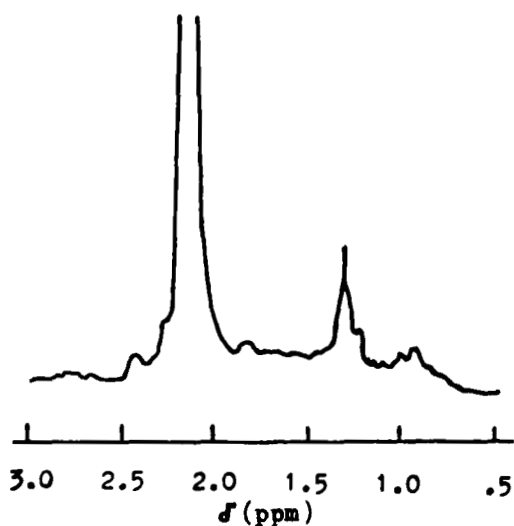


FIG. 10. H-NMR spectrum of PB-*b*-AA copolymer.



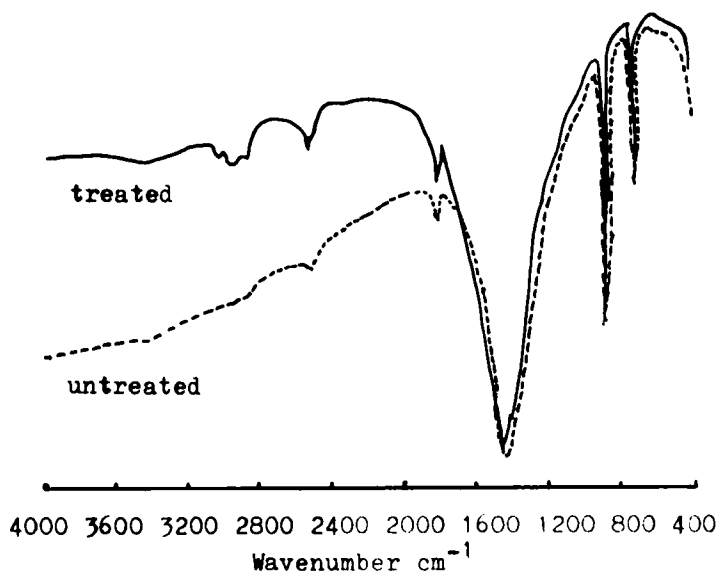


FIG. 11. IR spectrum of  $\text{CaCO}_3$  treated with PB-*b*-AA copolymer.

spite of the fact that the specimen has been thoroughly washed with water. This indicates that the copolymer is firmly held to  $\text{CaCO}_3$ , and that they are compatible.

The data listed in Table 1 show that in comparison with the silane coupling agent, and in spite of the amount of PB-*b*-AA used being only 1/15 of that of KH-550, both the mechanical properties and crosslinking density of the SBR filled with PB-*b*-AA treated  $\text{CaCO}_3$  are higher than that filled with silane coupling agent. Table 2 shows the coupling effect of PB-*b*-AA prepared under different irradiation time. The PB-*b*-AA ultrasonically prepared at 35°C, with a sonic intensity corre-

TABLE 1. Mechanical Properties of  $\text{CaCO}_3$ -Filled SBR<sup>a</sup>

Coupling agent	Amount of coupling agent used (g/100 g $\text{CaCO}_3$ )	Mechanical properties			Cross linking density $\times 10^1$
		Tensile strength (at 300% elongation), MPa	Breaking strength, MPa	Tearing strength, N/M	
Untreated		1.8	3.0	$9.0 \times 10^3$	5.19
PB- <i>b</i> -AA	0.1	2.7	4.6	$1.2 \times 10^4$	5.70
Silane coupling agent (KH-550)	1.5	1.9	3.3	$1.1 \times 10^4$	5.29

<sup>a</sup>SBR: oil-filled SBR, cured at 145°C under 15 MPa for 20 min.

TABLE 2. Coupling Effect of PB-*b*-AA Prepared at Different Irradiation Times in the SBR/CaCO<sub>3</sub> System<sup>a</sup>

Irradiation time, min	Amount of PB- <i>b</i> -AA (g/100 g CaCO <sub>3</sub> )	Mechanical properties				
		Tensile strength (300% elongation), MPa	Breaking strength, MPa	Tearing strength, N/M × 10 <sup>4</sup>	Breaking elongation, %	Permanent deformation, %
	0	2.23	4.50	1.72	525	26
40	0.1	3.74	6.14	1.97	450	15
80	0.1	3.84	6.26	3.80	420	15
120	0.1	3.44	7.25	1.97	568	20
160	0.1	2.74	7.13	1.93	540	20

<sup>a</sup>SBR: SBR-1500, cured at 145°C under 15 MPa for 20 min.

sponding to 370 W for a period of 80 min, is the best as the coupling agent for the SBR/CaCO<sub>3</sub> system. The tearing strength of the system is raised by 33–120%.

Figure 12 illustrates SEM microphotographs of the fracture surface of SBR filled with CaCO<sub>3</sub>. The interface between CaCO<sub>3</sub> and SBR is not sharply edged, indicating that they have good compatibility.

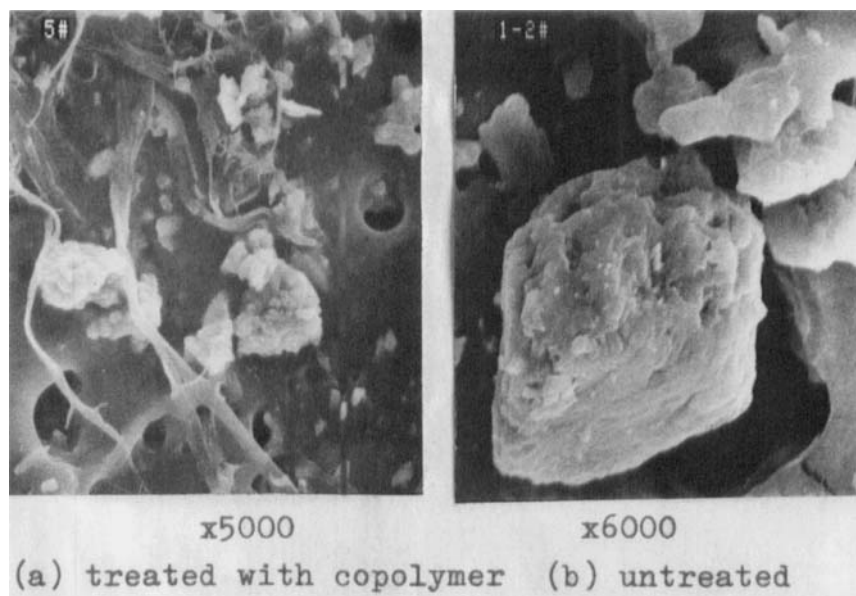


FIG. 12. SEM micrographs of tensile fractured surface of vulcanized SBR/CaCO<sub>3</sub> (100/70).

## CONCLUSIONS

1. The ultrasonic degradation of PB in cyclohexane solution follows the equation  $\overline{M}_t = (\overline{M}_0 - \overline{M}_\infty)e^{kt} + \overline{M}_\infty$ , where  $k = 33.33 \times 10^{-5} \text{ s}^{-1}$  (2% PB, 370 W, 35°C).

2. PB-AA copolymer can be prepared by ultrasonic degradation of PB which is then copolymerized with AA in cyclohexane solution. Both the yield of copolymer and its AA content increase with the amount of AA added, and the yield decreases with an increase in the reaction temperature. The block structure of the copolymer was identified by IR and NMR.

3. The mechanical properties of the SBR/CaCO<sub>3</sub> system are significantly improved. The tensile strength at 300% elongation and the breaking and the tearing strength of the SBR/copolymer treated with CaCO<sub>3</sub>, as compared with that of the untreated material are increased by 30–40, 40–50, and 33–120%, respectively.

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