

Improvement in Physical Properties of Poly(vinyl Chloride) by Radiation-Induced Graft Copolymerization with Mixed Monomers

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Synopsis

Gamma-ray-induced graft copolymerization of butadiene with vinyl monomers onto PVC was attempted to improve the physical properties of PVC. The Izod impact strength was increased from 2 kg-cm/cm² to more than 100 kg-cm/cm² by grafting ca. 10% butadiene. But the tensile strength and melt flow were decreased by the grafting. The electron micrograph showed that the mass of polybutadiene in the graft copolymer had a convenient diameter (0.1–1 μ) for absorbing the impact energy. The weatherability of PVC grafted with butadiene was improved by cograftering of butadiene with acrylates and methacrylates which had long side chains.

INTRODUCTION

In recent years, the impact strength of poly(vinyl chloride) (PVC) has been improved by blending with rubber polymers such as NBR,¹ SBR,² and chlorinated polyolefins.^{3,4} It was reported that appropriate adhesion between the rigid polymer and rubber or a chemical bond between them was necessary to produce a blend polymer of high impact strength.⁵ There was also a report that a blend polymer of PVC with rubber sometimes produced block or graft copolymers by a mechanochemical method such as roll mixing⁶. Another possible method to produce a chemical bond is radiation-induced graft copolymerization.⁷ For example, PVC is grafted with diene monomers by the irradiation of a mixture of PVC and monomer⁸ or by the preirradiation method.⁹

For the practical use of such blend polymers or graft copolymers, sufficient weatherability is required. That is, the impact strength must be retained for a sufficiently long period. For this purpose, the grafting of butadiene is not adequate because polybutadiene is easily photodecomposed¹⁰ and produces radicals which may attack PVC polymer chains and induce their decomposition. PVC is also photodecomposable. Several attempts to improve the stability of PVC by grafting of vinyl monomers or blending with their homopolymers were reported.¹¹

Thus, in this study radiation-induced graft copolymerization of butadiene with acrylates and methacrylates was attempted in order to produce PVC of high-impact strength even after a sufficient time interval in the weathering test.

EXPERIMENTAL

PVC powder (Chisso Co., Nipolit SL, D.P. 1050) was grafted with butadiene (Tonon Petro. Chem. Co., 99% purity) by ^{60}Co γ -rays in the gas phase. Polybutadiene (JSR BRO1) was supplied by Japan Synthetic Rubber Co.

The grafting apparatus is shown in Figure 1. Butadiene gas is introduced through the rotameter A-1 to the powder layer in the fixed-bed reactor (26 cm diam. \times 130 cm long), and the unreacted gas is exhausted through the rotameter A-2. The powder layer is agitated by the paddle-type blades B, and is thermostated by the water jacket C. The reaction temperature is 60°C. After a sufficient supply of butadiene gas in the powder layer (ca. 30 min), the ^{60}Co γ -ray source D is brought to the reactor and the reaction is started.

The dose rate at the center of the reactor was $1\text{--}6 \times 10^4$ rad/hr, which was measured by a Radocon (The Victreen Instrument Co.) The temperature in the powder layer was measured by C-A thermocouples. The grafting yield of butadiene was obtained from the weight increase because its homopolymer extracted with diethyl ether was always less than 3% of the total conversion of butadiene. The density of graft copolymer was measured by immersing the powder in the mixture of trichloroethane-methanol in various mixing ratios.

For the cografting of liquid monomers with butadiene, the PVC layer was swelled with the monomers which had been purified by distillation, and butadiene gas was then introduced. Typical monomers used in this study are styrene, methylmethacrylate (MMA), *n*-butyl methacrylate (*n*-BMA), and 2-ethylhexyl acrylate (2-EHA).

Two phr of dibutyltin maleate (Sankyo Organic Syntheses) was used as a stabilizer for the heat treatment of the graft copolymer. The graft sample was roll mixed at 185°C for 5 min and heat pressed at 185°C for 10 min.

Measurement of the physical properties of graft PVC was as follows: The Izod impact strength was measured with a Toyo Seiki Izod impact tester according to JIS K-6911 and by the falling ball method according to JIS K-6745. The tensile properties (tensile strength and elongation) were measured with a Shimadzu Autograph IS-2000 according to JIS K-6742. The melt flow was measured by means of a Koka flow tester (Shimadzu Type 301), where the increase in the sample temperature was 6°C/min and the pressure added to the sample

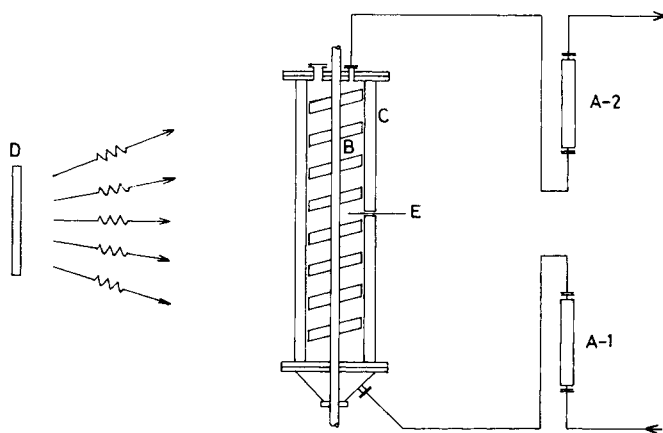


Fig. 1. Experimental apparatus. A-1, A-2, flow meter; B, blade; C, water jacket; D, γ -ray source; E, thermocouple.

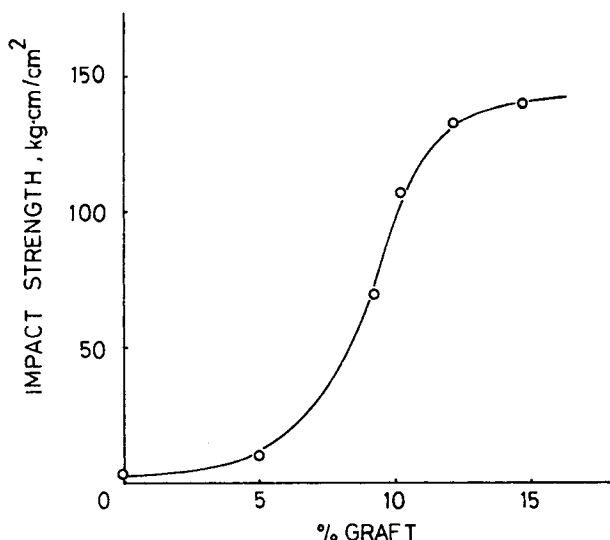


Fig. 2. Effect of grafting yield of butadiene on Izod impact strength of PVC-*g*-Bd at 20°C.

phase was 100 kg/cm². The weatherability was measured both by a xenon weathermeter (Suga Test Instr. Co., WE-6X-HC) and by outdoor exposure.

The electron micrographs of the graft copolymer and those of the blend polymer were obtained with a Japan Electron electron microscope Model JSM-U3.

RESULTS AND DISCUSSION

Physical Properties of Graft Copolymer

Figure 2 shows the effect of grafting yield of butadiene on the Izod impact strength of graft PVC (PVC-*g*-Bd). The maximum value of the impact strength at 20°C is 140 kg-cm/cm², which is 70 times that of the original PVC. This strength is sufficiently large even at -20°C, as shown in Table I. But the impact strength of PVC without grafting is decreased to ca. one seventh of the original at -20°C.

Nielsen⁵ said that the following three conditions were essential to produce a blend polymer of high impact strength by the combination of a rigid polymer and rubber: (1) T_g of the rubber component should be well below the test temperature; (2) there should be good adhesion between the two phases; (3) the

TABLE I
Izod Impact Strength of PVC and PVC-*g*-Bd at Various Temperatures

Temp., °C	Izod impact strength, kg-cm/cm ²	
	PVC	PVC- <i>g</i> -Bd ^a
20	2	107
0	2	100
-20	0.3	84

^a Percent graft = 10.2.

elastomeric material must form a second phase dispersed in the rigid polymer.

The grafting of butadiene onto PVC satisfies the former two conditions. That is, T_g of polybutadiene¹² is -107°C , which is almost 100°C lower than room temperature and the polybutadiene phase is chemically bonded to the PVC trunk polymer by the grafting procedure.

In order to clarify whether or not the graft copolymer satisfies the third condition, electron micrographs of graft copolymers were measured. Figure 3 shows the transmission electron micrographs of the slices of (a) PVC-*g*-Bd powder, (b) the sheet of PVC-*g*-Bd after roll mixing, and (c) the sheet of blend polymer of PVC with 10 phr of polybutadiene after roll mixing. In the former two cases, the grafting yield of butadiene is 15%. The black part of the photographs shows the polybutadiene part dyed with OsO_4 .¹³ Figure 3(b) shows that the diameter of the mass of polybutadiene is increased to the range of $0.1\text{--}1\ \mu$ by the procedure of roll mixing. Matsuo¹⁴ said that the high impact strength of PVC blended with rubber polymers such as ABS or MBS was due to the existence of rubber phase which had a convenient diameter for absorbing the impact energy. His explanation is as follows. The blend polymer is easily broken at the interface of the two components by a small impact when the rubber phase is poorly soluble in PVC phase and the rubber particle is large. The blend sample is also weak to the high-speed stress when the rubber phase is almost uniformly mixed with PVC phase and the rubber particle is small. When the rubber phase is slightly miscible with the PVC phase and the diameter of the polybutadiene particle is, for example, in the range of $0.1\text{--}1\ \mu$, the development of "stress crazing" absorbs the impact energy. In our case, the diameter of the polybutadiene mass happens to be in this preferable region for absorbing the impact strength, which will satisfy the third condition of Nielsen. On the contrary, the blend polymer which has only a similar impact strength as the original PVC¹⁵ shows a sharp interphase between the two phases of PVC and polybutadiene and most of the masses of polybutadiene are independent of one another as shown in Figure 3(c). This is disadvantageous to the development of the "stress crazing." Perhaps this blend system of PVC and polybutadiene applies to the first case of Matsuo's explanation.

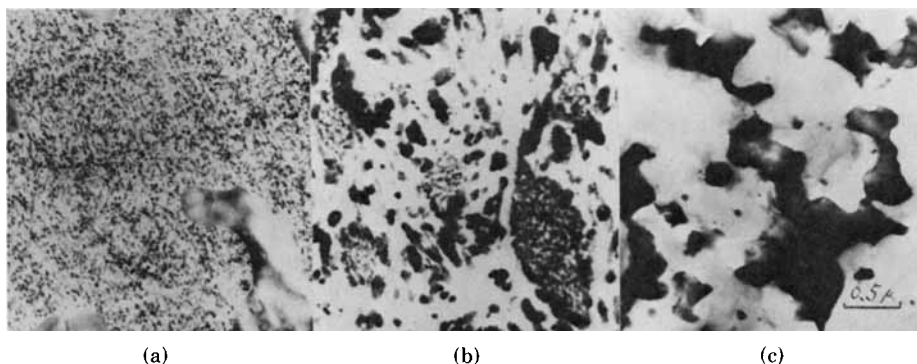


Fig. 3. Electron micrograph of (a) PVC-*g*-Bd powder and (b) PVC-*g*-Bd sheet after roll mixing, where the grafting yield is 15%, and (c) sheet of blend polymer of PVC with 10 phr of polybutadiene. Magnification is 30,000.

Figure 4 shows that the tensile strength is decreased continuously with increase in grafting yield of butadiene. These tendencies are often observed when rubber is added to a brittle polymer such as PVC and polystyrene at a temperature between the glass transition temperatures of the two components.⁵ The elongation of the graft copolymer is increased with the increase in the grafting yield like the impact strength as shown in Figure 4.

A steep decrease in the melt flow of PVC-*g*-Bd was observed by the Koka flow tester (Fig. 5). The melt flow of PVC has a connection with "flow unit" which is formed from several PVC particles fused together in the process of roll mixing,¹⁶ and even a small amount of crosslinking among these "flow units" will decrease the melt flow.

In order to clarify this possibility, the gel formation of graft PVC was studied. Table II shows the gel percent of graft PVC and the irradiated polybutadiene after the extraction with tetrahydrofuran which was a good solvent for both PVC and polybutadiene. The gel percent was 7.7% from PVC-*g*-Bd (grafting yield 5%), although no gel formation was observed from PVC-*g*-Bd (grafting yield 0.5%) and the gel percent from pure polybutadiene was only 18%. Thus, it is obvious

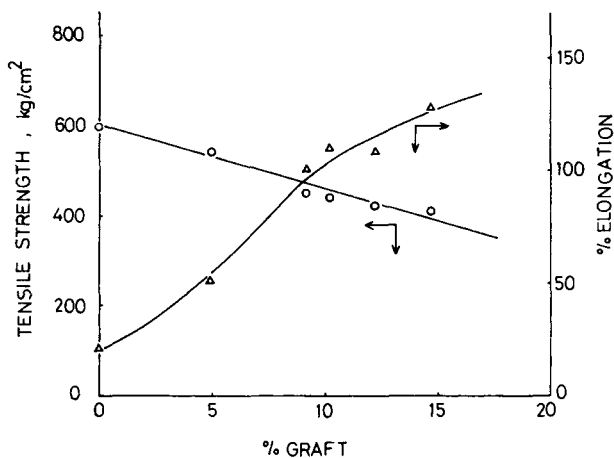


Fig. 4. Effect of grafting yield of butadiene on tensile properties of PVC-*g*-Bd.

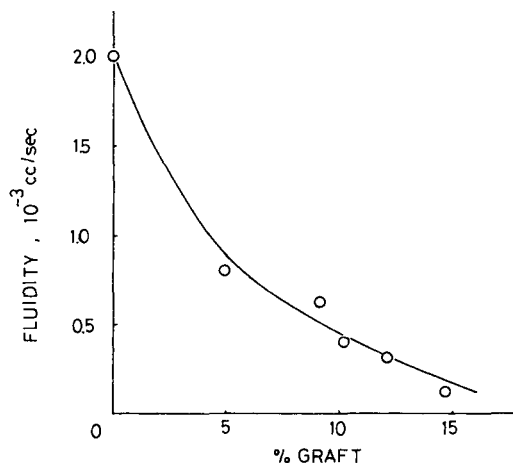


Fig. 5. Effect of grafting yield of butadiene on fluidity of PVC-*g*-Bd.

TABLE III
Calculation of Molar Attraction Constant and Average Molecular Weight of the Repeating Unit of PVC-*g*-(Bd-*co*-MMA)

	PVC (I)	Polybutadiene (II)	Poly(methyl methacrylate) (III)
Weight W	100	10	4
$d, \text{g/cm}^3$	1.42	1.00	1.19
M	62.5	54.1	100.1
$G-\text{CH}_3$			214×2
$-\text{CH}_2-$	133	133×2	133
$-\text{CH}=\text{C}-$	28	111×2	
$-\text{C}-$			-93
$-\text{Cl}$	270		
$-\text{C}(=\text{O})-\text{O}-$			310
ΣG	431	488	778

$$l = \frac{W_I/M_I}{W_I/M_I + W_{II}/M_{II} + W_{III}/M_{III}} = 0.877$$

$$m = \frac{W_{II}/M_{II}}{W_I/M_I + W_{II}/M_{II} + W_{III}/M_{III}} = 0.101$$

$$n = \frac{W_{III}/M_{III}}{W_I/M_I + W_{II}/M_{II} + W_{III}/M_{III}} = 0.022$$

$$\bar{M} = M_I l + M_{II} m + M_{III} n = 62.5$$

$$\overline{\Sigma G} = (\Sigma G)_I l + (\Sigma G)_{II} m + (\Sigma G)_{III} n = 444.4$$

monomer affected this value little, it is concluded that the graft copolymers used in this study have the same solubility parameters as the original PVC.

Figure 6 shows the decrease in impact strength of PVC-*g*-Bd, PVC-*g*-(Bd-*co*-St), PVC-*g*-(Bd-*co*-MMA), and PVC-*g*-(Bd-*co*-BMA) by exposure in the xenon weathermeter, where the grafting yield of butadiene is 10% and that of vinyl monomer is 3%, respectively. Although the decreasing curve of the impact strength of PVC-*g*-(Bd-*co*-MMA) is almost the same as that of PVC-*g*-Bd, the initial impact strength of the former is about 70% that of the latter, which is probably due to the rigidity of poly(methyl methacrylate). Because of the rigidity of polystyrene, the decrease in strength of PVC-*g*-(Bd-*co*-St) is larger than that of the others. On the other hand, PVC-*g*-(Bd-*co*-BMA) has the same initial strength as PVC-*g*-Bd, and its decrease is smaller than that of PVC-*g*-Bd. The value of T_g of poly(*n*-butyl methacrylate) is -24°C , which is much lower than that of the other vinyl monomers used. Thus, it is clear that the cografting of methacrylate whose homopolymer has a low glass transition temperature gives the rubber-like property to PVC and improves the weatherability of PVC-*g*-Bd.

Another example of the improvement of weatherability is the cografting of 2-EHA, which has also a long ester chain like *n*-BMA. The T_g of its homopolymer is -50°C . Figure 7 shows the effect of outdoor exposure on the impact strength of PVC-*g*-(Bd-*co*-2EHA) and PVC-*g*-Bd measured by the falling-ball test, where the grafting yield of butadiene is 10% and that of 2-EHA is 1%, respectively. The difference of the strength of these two graft polymers in the weathering test is prominent in the first four weeks, that is, the decreasing rate

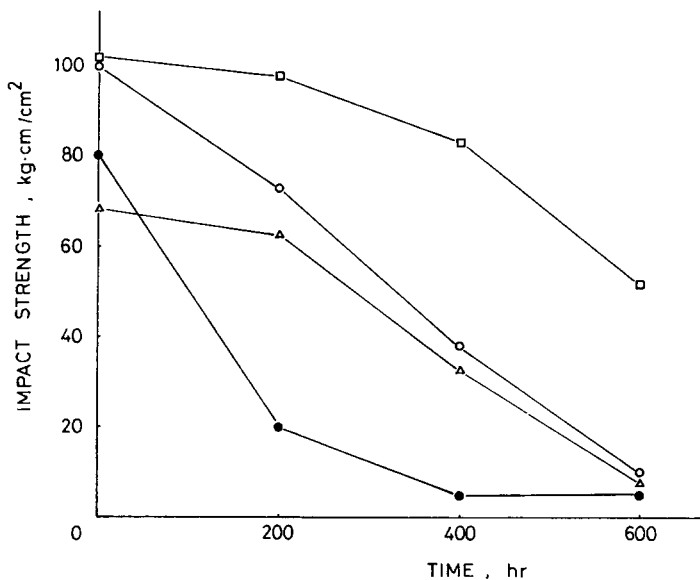


Fig. 6. Weathering test of (○) PVC-g-Bd, (●) PVC-g-(Bd-co-St), (Δ) PVC-g-(Bd-co-MMA), and (□) PVC-g-(Bd-co-BMA) by xenon weathermeter, where the grafting yield of butadiene is 10% and that of vinyl monomer is 3%, respectively.

of strength of PVC-g-(Bd-co-2EHA) is less than that of PVC-g-Bd, although no distinct differences of decreasing rates are observed after the four weeks. Thus, it is clear that the cografting of 2-EHA is also effective for the retention of high impact strength in the weathering test.

Both Figures 6 and 7 show the similar effects of cografting of methacrylate

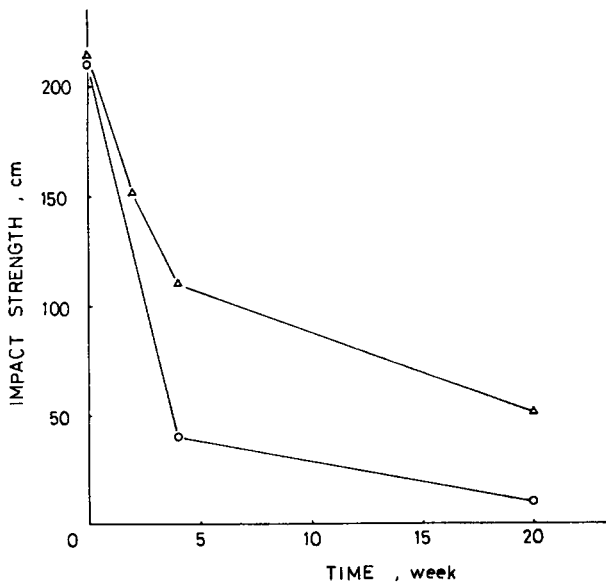


Fig. 7. Weathering test of (○) PVC-g-Bd and (Δ) PVC-g-(Bd-co-2EHA) by outdoor exposure, where the grafting yield of butadiene is 10% and that of 2-ethylhexyl acrylate is 1%. Impact strength was measured by the falling ball method.

or acrylate with long ester chains on the weatherability of the graft sample. That is, the existence of these acrylic or methacrylic components in the graft chain prevents the decrease in impact strength of the sample. Perhaps some of the energy exposed on the graft sample will be selectively absorbed by the carbonyl groups of acrylate or methacrylate and be consumed in the excitation or the scission of these ester groups,¹⁰ which will reduce such reactions as the chlorine atom elimination and the main chain scission of PVC and also the chain scission of polybutadiene.

It is concluded that the cograftering of butadiene with acrylate or methacrylate the homopolymer of which has a low glass transition temperature is useful for producing PVC of high impact strength even after a sufficient time interval in the weathering test.

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