Polymeric Reaction of Polymer-Monomer System Irradiated by Low Energy Electron Beam. III. Adhesive Property of Pressure Sensitive Adhesive

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Synopsis

Application of low-energy electron beam to nonsolvent-type pressure-sensitive adhesive is investigated. Adhesive properties such as peel strength, dead load strength, and ball tack were closely related to the reaction behavior (gel fraction and graft efficiency) of the acrylate polymer–monomer system. The reaction behavior is elucidated by combining the measurements of gel fraction, infrared spectrum of gel, and molecular weight distribution detected by gel permeation chromatography. It was found that the adhesive property of electro beam-cured adhesives depends on the molecular weight of added polymer, monomer concentration, and irradiation dose. Graft polymerization and moderate crosslinking by electron beam irradiation especially contribute to superior high adhesive properties.

INTRODUCTION

With the development of a low-energy electron beam (EB) accelerator, EB curing techniques can be applied to coating of steel,[1] gravure printing, coating and laminating of papers and films. Recently, the main purpose of introduction of EB technique tends to be not only for drying and curing, but also for improving mechanical and surface properties of the coating layer. This tendency is found in the application of coatings for magnetic tape and pressure-sensitive adhesives.[2] EB-cured pressure-sensitive adhesive was reported to have adhesive properties superior to that of conventional adhesive. There are two possible types of materials for EB curing adhesive. One is a prepolymer with multifunctional groups. Another one is a polymer–monomer system.

There are many investigations concerning the reaction behavior and the mechanical properties of general EB-influenced systems. The mechanical properties and the morphology of EB curing poly(urethane acrylate) were reported.[3-5] The reaction behavior at EB irradiation was investigated in the polyvinyl chloride-methacrylate monomer system in which it was reported that the crosslinking, the graft, and the homopolymerization occurred competitively.[6-11] We also reported that reaction behavior depended on the molecular weight of added polymer and the polymer-to-monomer ratio in the acrylate polymer-monomer system.[12,13] It has been shown that in the conventional adhesive, high-molecular weight polymers contribute to high peel strength and cohesive strength,[14] and that the peel strength of pressure-sensitive adhesive depends on peeling rate, peeling angle, molecular weight

of adhesive polymer, thickness of adhesive, and backing film.[15] However, there are few investigations on the relationship between the adhesive properties and the reaction behavior by EB irradiation. This study was performed to elucidate the relation between the adhesive properties and reaction behaviors such as crosslinking, graft, and homopolymerization in the acrylate polymer-monomer system. The manufacturing process of EB curing adhesives must be designed so that the high-molecular weight polymer system is produced by starting from the low-molecular weight polymer system since low viscosity is required for coating. We used poly(butyl acrylate) (PBA) as a polymer and diethylene glycol 4-nonyl phenyl ether acrylate (DNPA) as a monomer. Effects of molecular weight of added PBA, PBA-to-DNPA ratio, and irradiation dose on adhesive properties were examined.

EXPERIMENTAL

Preparation of Irradiation Sample

n-Butyl acrylate (n-BA) was polymerized in ethyl acetate at 76°C for 4 h using azobisisobutyronitrile and t-dodecyl mercaptan as an initiator and a chain transfer agent, respectively. The reaction mixture was poured into a large excess of methanol and hexane mixture. Poly(butyl acrylate) s with weight-average molecular weights of 2×10^4, 8×10^4, 10×10^4, 15×10^4, and 27×10^4 were obtained by addition of t-dodecyl mercaptan (t-DM) in the mole ratio of $[t$-DM$]/[n$-BA$] = 0.035, 0.02, 0.01, 0.007$, and 0.003, respectively. Monomer DNPA was a commercial-grade product (Toa Gosei Chemical Co., Ltd.) (Fig. 1). The polymer-monomer mixture was applied onto a poly(ethylene terephthalate) (PET) film (25μm).

Irradiation and Apparatus

Samples were irradiated under nitrogen at room temperature. A low energy (175 keV) electron beam irradiation apparatus (Energy Science, Inc.) which is an electrocurtain-type accelerator equipped with linear filament was used.

Adhesion Property Test

Peel Strength. Peel strength was measured at 20°C by peeling from clear stainless steel plate at an angle 180°, at a peel rate of 50 mm/min.

Dead Load Strength. Cohesive strength refers to internal strength of the adhesive mass, which resists the tendency to flow or creep under an applied load. The evaluation of this property is generally in the form of dead load test in which the bonded assembly is subjected to a constant stress (1 kg) and the time to failure is measured. A typical test design is shown in Figure 2. The test was carried out at 60°C under the accelerated condition to shorten the test time.

Ball Tack. Tack is a property of pressure-sensitive adhesive which intimately contacts a second surface to form an instantaneous bond. The tack is defined as the diameter of the smallest stainless ball which adheres to

$$CH_2=CHCOO(CH_2CH_2O)_n \langle\bigcirc\rangle C_9H_{19}$$
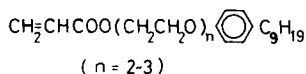
$$(n = 2\text{-}3)$$

Fig. 1. DNPA structure.

the adhesive surface when the balls with various diameters fall down the adhesive slope at angle 30° by Dow's method. A typical test design is shown in Figure 3. For example, ball Tack 10 means that 10/32 inch diameter of steel ball adheres to the surface.

Characterization of Reaction Products

Conversion of monomer was determined by weighing the polymer precipitated from methanol and hexane mixture. The Sol fraction was extracted by means of a Soxhlet extractor with refluxing ethyl acetate for 24 h. The insoluble part was defined as the gel fraction. The molecular weight was measured using gel permeation chromatography (GPC) equipped with both ultraviolet (UV) of 254 nm wavelength and refractive index (RI) detectors. Figure 4 shows the GPC curve of soluble part in the PBA-DNPA system after 5 Mrad irradiation (15.2 Mrad/s). The shoulder on the DNPA is due to an impurity. Before irradiation, DNPA peak could be detected by both UV and RI. Since PBA peak has no chromophore to be detected by UV, it is only detected by RI (dashed line). After irradiation, bimodal polymer peaks detected by UV were attributable to phenyl groups in the DNPA units. As described in the previous paper,[12] the peak which appeared at a higher molecular weight range in the UV-detected curves is possibly due to a graft polymer. The reasons are as follows: (1) The polymer-containing phenyl groups can be detected by UV. (2) The area of the UV-detected curve which appears at a high-molecular weight region increases with increasing irradiation dose. (3) The peak appearing at a low-molecular weight region is considered to be a homopolymer of DNPA, because the GPC curve of poly(DNPA) obtained by irradiating DNPA to 5 Mrad appears at the same region as the UV-detected low-molecular weight peak. The graft efficiency
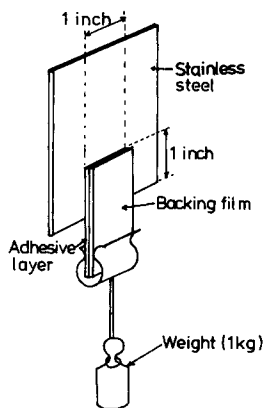
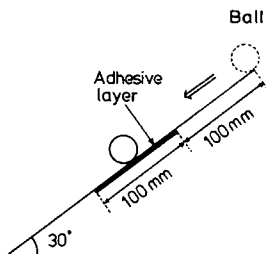Fig. 2. A typical design of dead load strength.

Fig. 3.   A typical test design of ball tack.

of the soluble fraction was estimated using the GPC curve by the following equation.

$$\text{Graft efficiency (\%)} = \frac{\text{peak area of graft polymer}}{\text{peak area of UV-detected polymer}}$$

In Figure 5 are shown of a PBA homopolymer, the gel obtained from the 1:0.5 PBA-DNPA system after 5 Mrad irradiation, and poly(DNPA). The percent DNPA units incorporated into the gel was calculated by using the calibration curve, obtained by measurement of the IR absorbance of the phenyl group of poly(DNPA) at 1600 cm^{-1} to the carbonyl group of polymers at 1730 cm^{-1}, as shown in Figure 6. The infrared spectra were obtained from free-standing films.

RESULT AND DISCUSSION

Effects of Molecular Weight of Added PBA

The dependence of reaction behavior (gel fraction, DNPA units into gel, DNPA conversion, graft efficiency, and weight average molecular weight) and adhesive properties (peel strength, dead load strength, and tack) on the
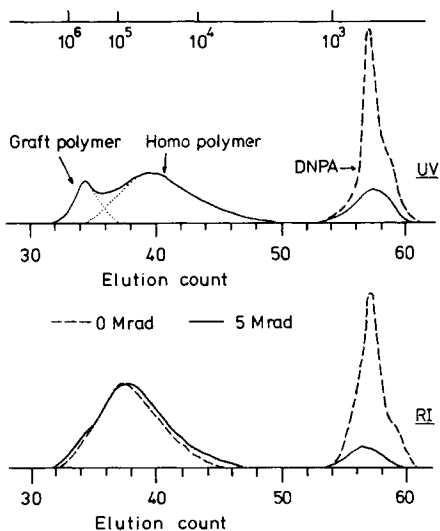

Fig. 4.   GPC curves of soluble part in the 1:0.5(w/w)PBA-DNPA system irradiated to 5 Mrad.
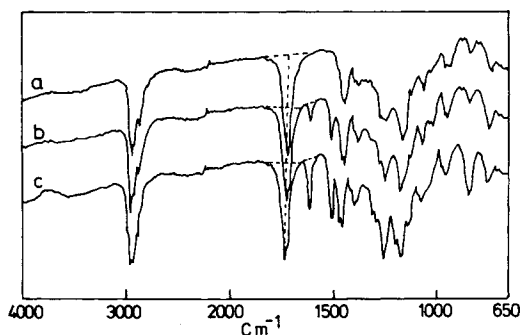
Fig. 5. IR spectra of (a) PBA, (b) gel from the 1:0.5 PBA–DNPA system after 5 Mrad irradiation, (c) poly(DNPA).

molecular weight of added PBA was examined after 5 Mrad irradiation. The results were summarized in Table I. With increasing molecular weight of added PBA, the gel fraction and graft efficiency increased, while the DNPA units into gel decreased. The conversion was independent of the molecular weight of added PBA (72–79%). The molecular weights of soluble parts were higher than that of the added PBAs, except for the case of PBA with high-molecular weight of 27×10^4, because the molecular weight of the soluble parts indicates the average molecular weight of a polymer mixture containing unreacted PBA, high-molecular weight graft polymer, and low-molecular weight of DNPA homopolymer. It was found that such adhesive properties as peel strength, dead load strength, and tack also increased with increasing molecular weight of the added PBA. The reaction behavior (gel fraction, DNPA units in gel, and graft efficiency) and the adhesive properties (peel strength and dead load strength) in Table I are plotted against the molecular weight of added PBA in Figure 7 and 8. As shown in Figure 7, in the PBA (MW more than 10×10^4)-DNPA system, the graft efficiency increased with the molecular weight of added PBA, but the DNPA units in gel decreased from 44% to 14%. The results indicate that in the high-molecular weight PBA system, the crosslinking and the graft polymerization occur predominantly and DNPA units are incorporated in a large amount into soluble graft polymer rather than crosslinked polymer. As shown in Figure 8, the peel strength and the dead load strength increased with increasing molecular weight of added PBA and reached 490 g/15 mm and 122 min, respectively. Both also increased to a great extent
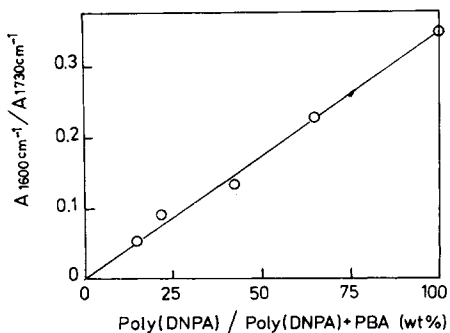

Fig. 6. Calibration curve calculating DNPA units incorporated into gel.

TABLE I
Dependence of Reaction Behavior and Adhesive Properties on the Molecular Weight of Added PBA in the 1:0.5 (w/w) PBA-DNPA System[a]

No.	$\overline{M}w$ of added PBA ($\times 10^4$)	Gel (%)	Gel — DNPA unit in gel (%)	Conv. (%)	Soluble part — Graft efficiency (%)	Soluble part — $\overline{M}w^b$ ($\times 10^4$)	Adhesive properties — Peel strength[c] (g/15 mm)	Adhesive properties — Dead load strength[d] (min)	Tack[e]
1	2.1	21	44	79	5	5.1	63	0	5
2	7.8	33	33	77	9	8.2	167	19	5
3	10.2	39	25	77	21	15.8	300	42	7
4	15.4	53	15	75	27	17.3	403	60	9
5	27.0	60	14	72	29	25.6	485	122	12

[a] EB irradiation, 5 Mrad. Monomer, $CH_2=CHCOO(CH_2CH_2O)_n$⬡C_9H_{19} (n=2~3)(DNPA).
[b] $\overline{M}w$ of soluble polymer was calculated by GPC(RI).
[c] Peel strength was measured at 20°C by peeling from steel plate at an angle 180°, in the peel rate of 50 mm/min.
[d] Dead load strength was measured by the following condition: temp. 60°C; deadload, 1tkg/in².
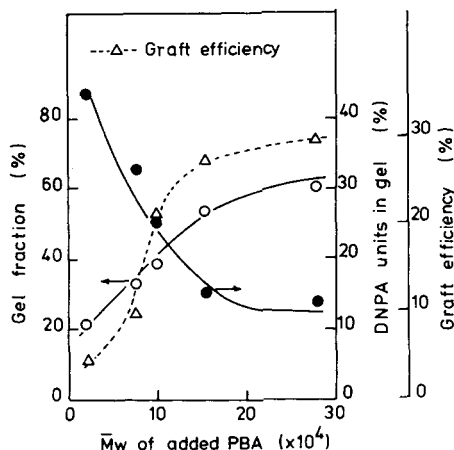[e] Tack was determined by Dow's method.

Fig. 7.   Gel fraction, DNPA units in gel, and graft efficiency as function of molecular weight of added PBA in the 1:0.5 PBA-DNPA system after 5 Mrad irradiation.

when the molecular weight of added PBA was more than 10×10^4. The comparison of the adhesive data in Figure 8 with the reaction behavior data in Figure 7 suggests that the formation of the graft polymer including PBA and DNPA units and of the cross-linked polymer including PBA and a small amount of DNPA contributes to the increase in peel strength and dead load strength.

As shown in Figure 9, ball tack as well as the adhesive strength increased with increasing molecular weight of the added PBA at 5 and 10 Mrad (30.4 Mrad/s) irradiation.

Effects of Polymer-to-Monomer Ratio

The wt% of DNPA in the PBA–DNPA system was varied at 5 Mrad irradiation. The results of the reaction behavior and the adhesive properties were summarized in Table II. The weight percent of DNPA was varied with
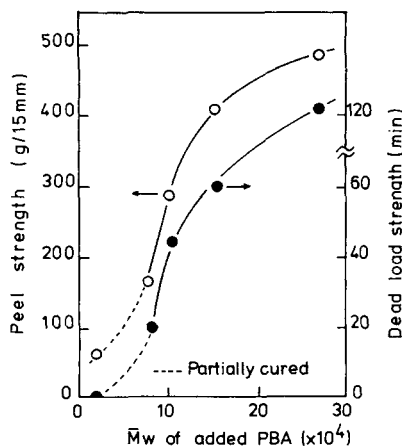

Fig. 8.   Peel strength and dead load strength as function of molecular weight of added PBA in the 1:0.5 PBA-DNPA system after 5 Mrad irradiation.
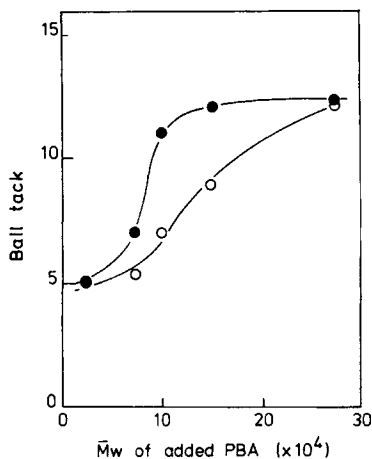
Fig. 9.   Ball tack (Dow's method) as function of molecular weight of added PBA in the 1:0.5 PBA-DNPA system. (—○—5 Mrad,—●—10 Mrad)

the reaction behavior and the adhesive properties after 5 Mrad shown in Table II. This data is shown in Figure 10 and 11 plotted as a function as weight percent DNPA. As shown Figure 10, with increasing wt% of DNPA, the gel fraction and the DNPA units in gel increased, while the graft efficiency decreased. When the wt% of DNPA is low, in the range of 15–25%, the graft polymerization predominates over the other reactions. On the other hand, in high wt% of DNPA, the crosslinking and the homopolymerization occur predominantly. The DNPA units must have been incorporated into the cross-linked polymer and the soluble homopolymer. As shown in Figure 11, the peel strength and dead load strength were highest in the 25–30 wt% DNPA system (peel strength, 350 g/15mm; dead load strength, 50 min). When the DNPA concentration was less than 25%, low adhesive strengths were obtained, which may be ascribed to low gel fraction in spite of high graft efficiency. On the other hand, in the case of more than 33%, DNPA concentration low adhesive strength may be due to low graft efficiency in spite of high gel fraction. As a result, it was found that to attain a superior adhesive property, a proper concentration of DNPA is necessary unless a high-molecular weight PBA is used. It was revealed that the high adhesive strength is caused by high proportions of both crosslinking and graft polymerization in this case.

As shown in Figure 12, the ball tack slightly decreased with increasing wt% of DNPA, and depended considerably on molecular weight of the added PBA. In the case of high-molecular weight PBA system ($\overline{M}w = 27 \times 10^4$), high ball tack was obtained. It is known that in the conventional acrylic pressure-sensitive adhesive (solution, hot melt, or emulsion type), the adhesive composed of a high-molecular weight polymer shows high cohesive strength but low tack. The comparison between the conventional adhesive and the EB cured adhesive indicates that in the latter, the remaining DNPA monomer and homopolymer of DNPA may reduce the tack. The reason for this being that the ball tack slightly decreased with increasing wt% of DNPA in the PBA-DNPA systems which, relates to the increase in the proportion of DNPA homopolymer and that the ball tack decreased in the

TABLE II
Dependence of Reaction Behavior and Adhesive Properties on the Weight Percent of DNPA in the PBA-DNPA System[a]

No.	Wt% of DNPA (%)	Gel		Soluble part			Adhesive properties		
		Gel (%)	DNPA units in gel (%)	Conv. (%)	Graft efficiency (%)	$\overline{M}_w$[b] ($\times 10^4$)	Peel strength[c] (g/15 mm)	Dead load strength[d] (min)	Tack[e]
1	17	29	21	75	27	13.8	154	5	8
2	23	33	20	77	28	15.9	350	45	7
3	30	36	24	79	23	16.4	345	51	7
4	33	39	25	77	21	15.8	300	42	7
5	50	57	36	84	12	10.1	163	14	6

[a] EB irradiation, 5 Mrad $\overline{M}_w$ of added PBA, 10.2×10^4. Monomer $CH_2=CHCOO(CH_2CH_2O)_n$ ⟨benzene ring⟩ C_9H_{19} (n = 2~3)(DNPA).
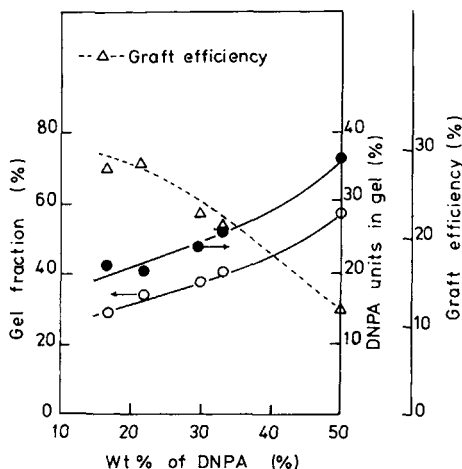[b]~e) The same as in Table I.

Fig. 10. Gel fraction, DNPA units in gel and graft efficiency as function of weight percent of DNPA at 5 Mrad irradiation. Mw of added PBA, 10×10^4.

low wt% DNPA system with high-molecular weight PBA, which relates to higher proportion of the remaining DNPA.

Effects of Irradiation Dose

The reaction behavior and the adhesive properties of the PBA ($\overline{M}w = 10 \times 10^4$)–DNPA system and the PBA ($\overline{M}w = 27 \times 10^4$)–DNPA system are summarized in Tables III and IV, respectively. The reaction behavior (gel fraction, DNPA units in gel, and graft efficiency) data in Tables III and IV were plotted against irradiation dose in Figures 13 and 14, respectively. As shown in Fig. 13, both gel fraction and graft efficiency increased with increasing dose, while DNPA units in gel decreased with increasing dose.
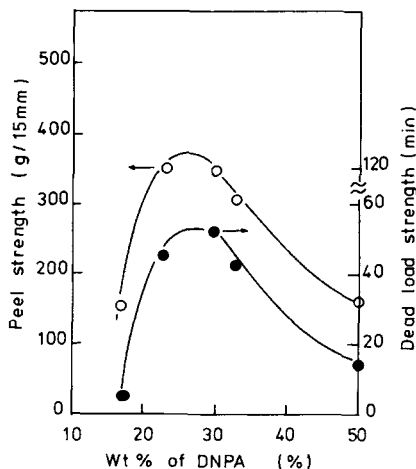

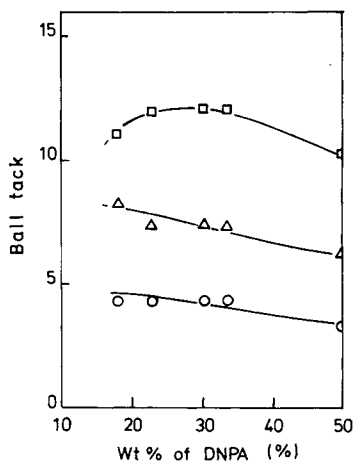Fig. 11. Peel strength and dead load strength as function of weight percent of DNPA at 5 Mrad irradiation. Mw of added PBA, 10×10^4.

Fig. 12. Ball tack (Dow's method) as function of weight percent of DNPA at 5 Mrad irradiation. —○—, 2 × 10^4, —△—, 10 × 10^4, —□—, 27 × 10^4.

This tendency is similar to that of dependence of the reaction behavior on the molecular weight of added PBA. Therefore, the adhesive properties are expected to be similar to that of Figure 8.

In Figure 14, the gel fraction increased with increasing dose, and the graft efficiency is the highest at approximately 7 Mrad. The DNPA units in gel was independent of the irradiation dose. The difference between Figures 13 and 14 is in the decrease of graft efficiency in higher doses than 5 Mrad. This phenomenon may be due to incorporation of graft polymer into gel, since the graft polymer with very high molecular weight may be inclined to become an insoluble polymer.

The peel strength and dead load strength data in Tables III and IV are plotted against irradiation dose in Figure 15. In the system having PBA molecular weight of 10 × 10^4, the adhesive strength increased with increasing dose as previously predicted. When high-molecular weight (27 × 10^4) PBA is used, the adhesive strength was the highest at 5 Mrad irradiation. These results indicate that the graft polymer contributed to high adhesive strengths and that a too densely cross-linked polymer reduced the adhesive strength, since the high adhesive strength was caused by satisfying both graft efficiency of more than 30% and gel fraction of less than 70%.

From these results, it was revealed that the adhesive strength of EB-curing pressure-sensitive adhesive depends on the molecular weight of added PBA, the concentration of DNPA monomer, and the irradiation dose. Moreover, EB curing adhesive with high adhesive strengths must contain the added PBA with molecular weight of more than 10 × 10^4. This is because that polymer chains with molecular weight of more than 10 × 10^4 may be apt to entangle themselves and it is this entanglement enhanced by graft polymerization and the crosslinking which contribute to high peel strength and dead load strength. In addition, the graft polymer is considered to contribute to the increase in solubility of homopolymer (poly(DNPA)), since in the high graft efficiency system, which was realized, for example,

TABLE III
Dependence of Reaction Behavior and Adhesive Properties on the Irradiation Dose in the 1:0.5 (w/w) PBA ($\overline{M}w = 10 \times 10^4$)-DNPA System[a]

No.	Dose (Mrad)	Gel (%)	DNPA unit in gel (%)	Conv. (%)	Soluble part Graft efficiency (%)	$\overline{M}_w$[b] ($\times 10^4$)	Adhesive properties Peel strength[c] (g/15mm)	Dead load strength[d] (min)	Tack[e]
1	3	32	27	60	13	14.7	108	10	5
2	5	39	25	77	21	15.8	300	42	7
3	7.5	50	23	85	25	16.5	352	60	10
4	10	53	21	87	33	15.2	425	115	12

[a] Monomer, $CH_2=CHCOO(CH_2CH_2O)_n$—⬡—C_9H_{19} (n=2~3)(DNPA).
[b~e] The same as in Table I.

TABLE IV

Dependence of Reaction Behavior and Adhesive Properties on the Irradiation Dose in the 1:0.5 (w/w) PBA ($\overline{M}w = 27 \times 10^4$)-DNPA System[a]

No.	Dose (Mrad)	Gel		Soluble part			Adhesive properties		
		Gel (%)	DNPA unit in gel (%)	Conv. (%)	Graft efficiency (%)	$\overline{M}w$ ($\times 10^4$)	Peel strength[c] (g/15 mm)	Dead load strength[d] (min)	Tack[e]
1	3	48	16	48	20	34.5	463	68	10
2	5	60	14	72	29	25.6	485	122	12
3	7.5	71	16	76	30	23.8	405	116	12
4	10	80	13	79	24	22.4	338	30	9

[a-e] The same as in Table III.
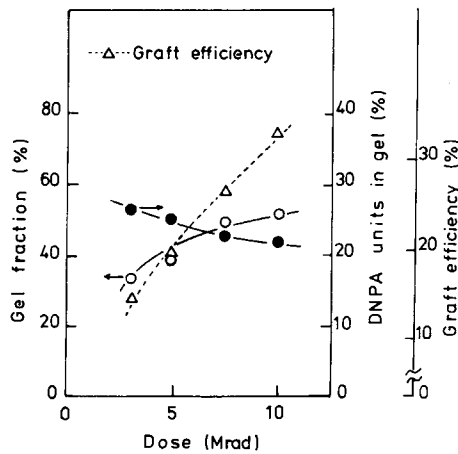
Fig. 13. Gel fraction, DNPA units in gel, and graft efficiency as function of irradiation dose in the 1:0.5 PBA (Mw = 10 × 10⁴)-DNPA system.

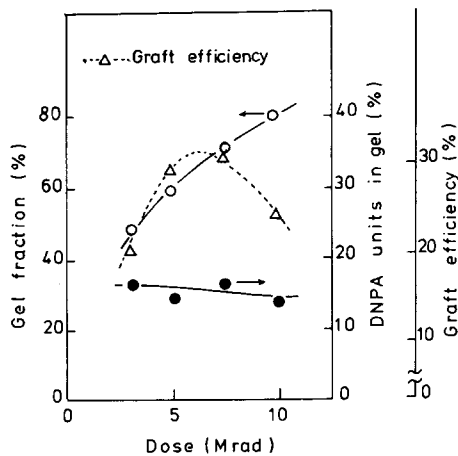Fig. 14. Gel fraction, DNPA units in gel, and graft efficiency as function of irradiation dose in the 1:0.5 PBA (Mw = 27 × 10⁴)-DNPA system.

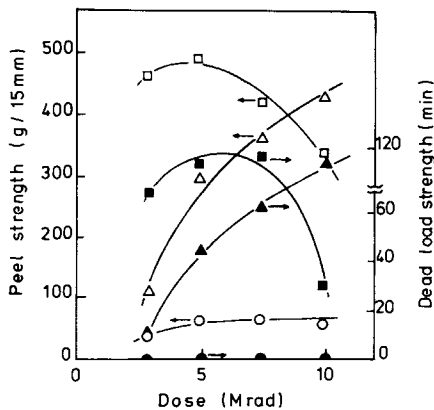Fig. 15. Peel strength and dead load strength as function of irradiation dose in the 1:0.5 PBA-DNPA systems.—○—, Mw = 2 × 10⁴, —△—, Mw = 10 × 10⁴, —□— Mw = 27 × 10⁴.

in the low wt% of DNPA system, the homopolymer was compatible with an unreacted PBA. Furthermore, in the high-molecular weight PBA system irradiated at high irradiation dose, a too dense crosslinking reduced the adhesive strength. Finally, it was concluded that without using a very high-molecular weight PBA, the adhesive with high adhesive strength can be obtained by accomplishing a proper combination of three factors, that is about 35–45% gel fraction, 20–25% DNPA units in gel, and 20–25% graft efficiency.

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