

# Polymeric Reaction of Polymer–Monomer System Irradiated by Low-Energy Electron Beam. IV. Adhesive Properties of Pressure Sensitive Adhesive

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## Synopsis

Electron beam (EB) preparation and properties of pressure sensitive adhesives were investigated. The pressure-sensitive adhesive was obtained by EB irradiation of a mixture of poly (butyl acrylate) (PBA) modified by acryloyl groups and 2-[2-hydroxy-3-phenoxy-propoxy]ethyl acrylate (HPA). For the polymer with molecular weight ( $\bar{M}_w$ ) of  $10 \times 10^4$ , the introduction of two acryloyl groups per polymer molecule had the highest peel and dead load strength. On the other hand, for the polymer with  $\bar{M}_w$  of  $3 \times 10^4$ , five acryloyl groups per polymer gave highest adhesive properties. This difference might be attributed to the entanglement of polymers with high molecular weights. Furthermore, the effect of the addition of polar monomers to the monomer mixture was investigated. Polar groups, such as hydroxyl and carboxyl groups, increased the adhesive properties.

## INTRODUCTION

Since a low energy electron beam accelerator can be conveniently used in a laboratory, many investigations on its applications have appeared in the field of the EB polymerization. There were some investigations of mechanical properties and morphology of EB cured poly(urethane acrylate) for a coating.<sup>1-3</sup> Several investigations have been published on the reaction behavior of poly(vinyl chloride)–methacrylate monomer system for crosslinking of wire insulation.<sup>4-9</sup> We also reported the reaction behavior of polymer–monomer systems.<sup>10,11</sup>

There are many applications which have been commercialized, or are on the verge of industrialization. For example, abrasive resistant coating for paper, plastic film, and steel,<sup>12</sup> adhesive for metallized paper,<sup>13</sup> magnetic media,<sup>14,15</sup> and silicone release paper and film have been already manufactured on a commercial basis.

However, EB cured pressure-sensitive adhesives have not been commercialized in spite of the several reports.<sup>16-18</sup> The major reason seems to be that in production of pressure-sensitive adhesives, advantages of EB cure over ultraviolet (UV) and thermal cures have not been found. Thus, in order to identify the advantages of pressure-sensitive adhesives by EB irradiation, we have studied the relationship between the adhesive properties and the reaction behavior of EB curing for one polymer–monomer system.<sup>19</sup> It has been revealed that

TABLE I  
 Copolymerization of BA with HEA

Run no.	Feed		Copolymer	
	[HEA]/[BA] ( $\times 10^{-3}$ )	[HEA]/[BA] <sup>a</sup> ( $\times 10^{-3}$ )	$\bar{M}_w$ ( $\times 10^4$ )	$\bar{M}_n$ <sup>b</sup> ( $\times 10^4$ )
P-1	0	0	9.5	4.1
P-2	6.0	5.1	11.7	5.4
P-3	9.0	8.2	11.0	5.0
P-4	25.0	23.4	12.5	5.5
P-5	160.0	142.9	11.0	5.0
P-6	0	0	2.5	0.9
P-7	50.0	48.1	2.8	1.2
p-8	75.0	75.0	3.4	1.3
p-9	200.0	189.3	3.1	1.2

<sup>a</sup> Determined by <sup>1</sup>H-NMR.

<sup>b</sup> Measured by GPC.

grafting and moderate crosslinking reactions caused by EB irradiation contribute to improved adhesive properties. It has also been shown that an increase in the molecular weight of the polymer increases the adhesion. In the conventional (thermal cure) pressure-sensitive adhesive, it has been also shown that high-molecular-weight polymers provide high peel and cohesive strength.<sup>20,21</sup> The manufacturing process of EB cured pressure-sensitive adhesives must be designed so that a high molecular weight polymer mixture is obtained by starting from a low-molecular-weight polymer system, since low viscosity is required to coat films with the pressure-sensitive adhesive solution.

In this paper, we wish to report the synthesis of adhesives consisting of poly(butyl acrylate) (PBA) modified by acryloyl groups as the polymer and

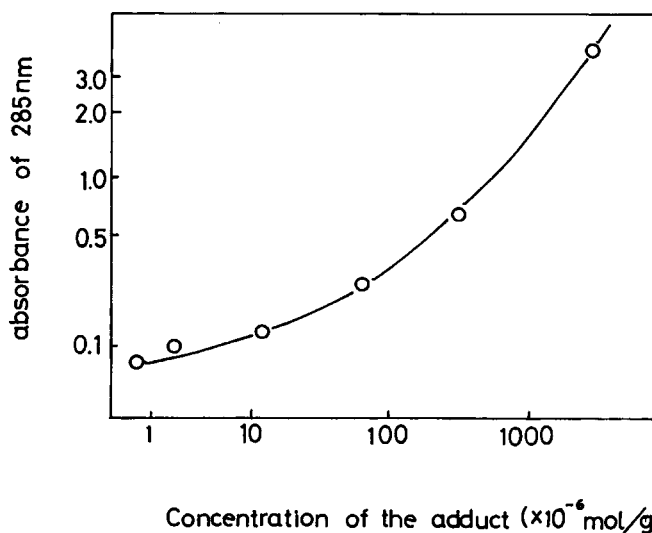


Fig. 1. Calibration curves calculating acryloyl group content of polymer.

TABLE II  
Characteristics of PBA-Containing Acryloyl Groups

Polymer no.	$\bar{M}_w (\times 10^4)$	$\bar{M}_n^a (\times 10^4)$	Content of acryloyl group	
			Concn <sup>b</sup> (mol/g) ( $\times 10^{-6}$ )	Number <sup>c</sup> (number/polymer)
M-1	10.1	4.3	0	0
M-2	12.5	6.0	31	1.9
M-3	11.3	5.2	48	2.5
M-4	13.0	6.0	118	7.1
M-5	11.4	5.4	894	48.3

<sup>a</sup> Measured by GPC.

<sup>b</sup> Determined by UV spectra at 285 nm.

<sup>c</sup> Number of acryloyl group/polymer = concn  $\times \bar{M}_n$ .

2-hydroxy-3-phenoxypropyl acrylate (HPPA) as the monomer. The effect of acryloyl group content on adhesive properties was investigated.

## EXPERIMENTAL

### Monomer

Butyl acrylate (BA), 2-hydroxyethyl acrylate (HEA) (Junsei Chemical Co. Ltd.), 2-hydroxy-3-phenoxypropyl acrylate (HPPA), 2-carboxyethyl acrylate (CEA) (Toa Gosei Chemical Co. Ltd.), 1,6-hexanediol diacrylate (HDDA), pentaerythritol triacrylate (PETA) (Nihon Kayaku Co. Ltd.), and phenoxyethyl acrylate (PEA) (Kyoisha Co. Ltd.) were used as monomers.

### Preparation of Polymer

#### Copolymer Synthesis

Copolymerization was carried out in a three-neck round bottomed flask. The reaction flask containing ethyl acetate, was maintained at 75°C under nitrogen, and a mixture of comonomers, azobis (isobutyronitrile) (AIBN), and *t*-dodecyl mercaptan (*t*-DM) was added dropwise (1 mL/min). The mole ratio of [HEA]/[BA] varied with the desired copolymer composition. The ratios of [AIBN]/[comonomer] and [*t*-DM]/[comonomer] were 0.02 and 0.01, respectively. After 4 h reaction, the resulting product was precipitated in a large amount of methanol and dried under vacuum. The weight-average molecular weight of the copolymer was about  $10 \times 10^4$ . When the ratios of [AIBN]/[comonomer] and [*t*-DM] were 0.04 and 0.02, respectively, copolymer with low molecular weight was obtained. Mole ratios of [HEA]/[BA] of the copolymers were measured by <sup>1</sup>H-NMR. Table I shows the mole ratio and the molecular weight of copolymers.

#### *Synthesis of Poly(n-butyl acrylate) Modified with HEA-TDI Adduct (Modified PBA)*

An equimolar amount of HEA (1.18 g) was added dropwise to 2,4-toluene diisocyanate (TDI) (1.74 g) under a nitrogen atmosphere. The temperature

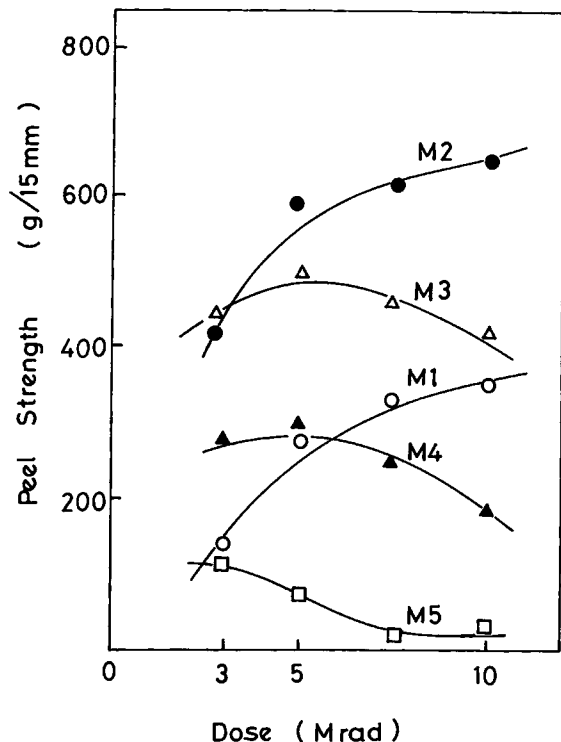


Fig. 2. Peel strength as function of irradiation dose in the PBA with various content of acryloyl groups-HPPA system. (The ratio of polymer/monomer = 2,  $\bar{M}_w$  of polymer =  $10 \times 10^4$ .)

was kept below 45°C to avoid thermal polymerization of acryloyl groups. When the temperature of the TDI/HEA reaction mixture started to drop, a stoichiometric quantity of poly(BA-co-HEA) was added along with dibutyltin dilaurate. The mixture was stirred for 1 h and heated to 70°C. The acryloyl group content of the polymer was determined by measuring the UV absorbance at 285 nm. This was compared to the calibration plot obtained by measuring absorbance of various concentrations of HEA-TDI-methanol mixtures, as shown in Figure 1.

#### Irradiation Condition

Samples were irradiated under nitrogen at room temperature. A low energy electron beam (200 kV) was used.

#### Adhesion Properties

**Peel Strength.** Poly(ethylene terephthalate) (PET) film was used as the substrate. The adhesive was applied onto the film and cured. The adhesive film was cut into 15 mm width and bonded onto a stainless steel plate. Peel strength was measured at 20°C by peeling from stainless plate at an angle of 180°, at a peel rate of 50 mm/min.

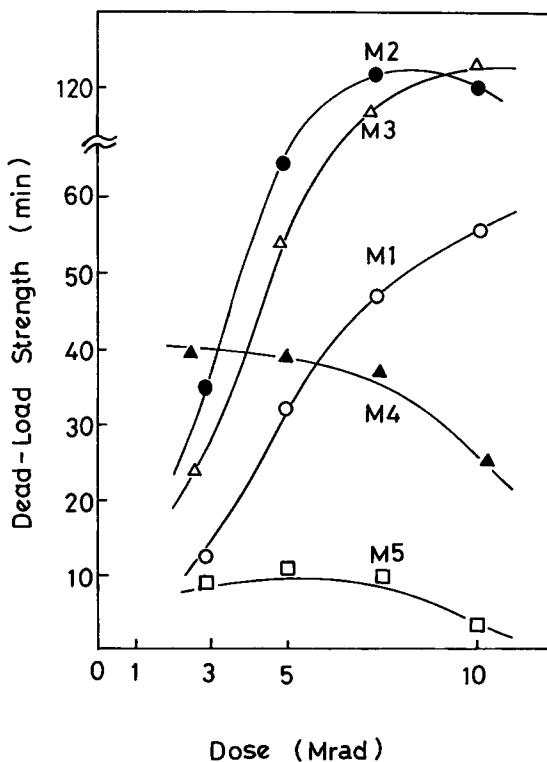


Fig. 3. Dead load strength as function of irradiation dose in the PBA with various content of acryloyl groups-HPPA system. (The ratio of polymer/monomer = 2,  $\bar{M}_w$  of polymer =  $10 \times 10^4$ .)

**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 carried out 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. The typical test design was reported earlier.<sup>19</sup> The adhesive film was cut into 1 in. width and bonded onto stainless steel plate with 1 in.<sup>2</sup> of adhesive area. A weight (1 kg) was hung down at the edge of the adhesive film. The test was carried out at 60°C under an accelerated condition to shorten the test time.

### Characterization of Reaction Products

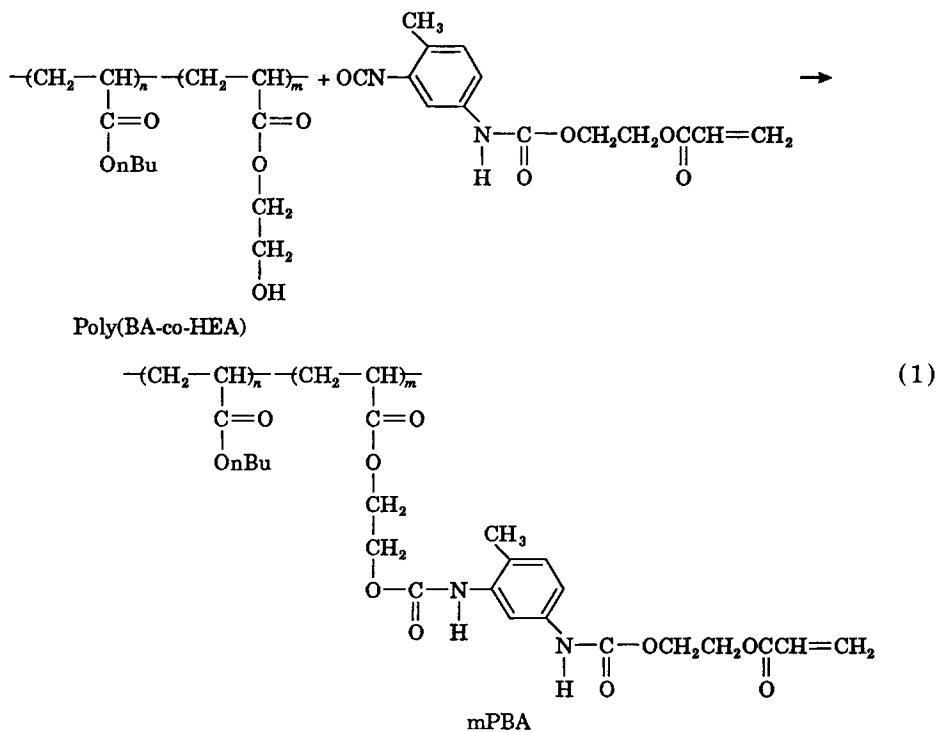
The reaction product was subjected to extraction by means of a Soxhlet extractor with refluxing ethyl acetate for 24 h. The weight percent of insolubles was defined as the gel fraction. The molecular weight was measured using a gel permeation chromatograph (GPC) equipped with both UV and RI detectors.

### Irradiated Sample

The polymer-monomer mixture was applied onto a poly(ethylene terephthalate) (PET) film with about 25 g/m<sup>2</sup>. The polymer-to-monomer weight ratio was 2 : 1.

## RESULTS AND DISCUSSION

Polyacrylates containing pendant acryloyl groups were synthesized according to



Four modified poly(*n*-butyl acrylate) (abbreviated as mPBA) based on the higher  $\bar{M}_w$  copolymer were prepared, in which each polymer molecule contains on average 1.9, 2.5, 7.1, and 48.3 acryloyl groups, respectively (see Table II).

TABLE III  
Characteristics of PBA-Containing Acryloyl Groups

Polymer no.	$\bar{M}_w$ ( $\times 10^4$ )	$\bar{M}_n^a$ ( $\times 10^4$ )	Content of acryloyl group	
			Concn <sup>b</sup> (mol/g) ( $\times 10^{-6}$ )	Number <sup>c</sup> (number/polymer)
M-6	2.7	1.0	0	0
M-7	3.0	1.2	258	3.1
M-8	3.5	1.4	400	5.6
M-9	3.3	1.4	1107	15.5

<sup>a</sup> Measured by GPC.

<sup>b</sup> Determined by UV spectra at 285 nm.

<sup>c</sup> Number of acryloyl group/polymer = concn  $\times \bar{M}_n$ .

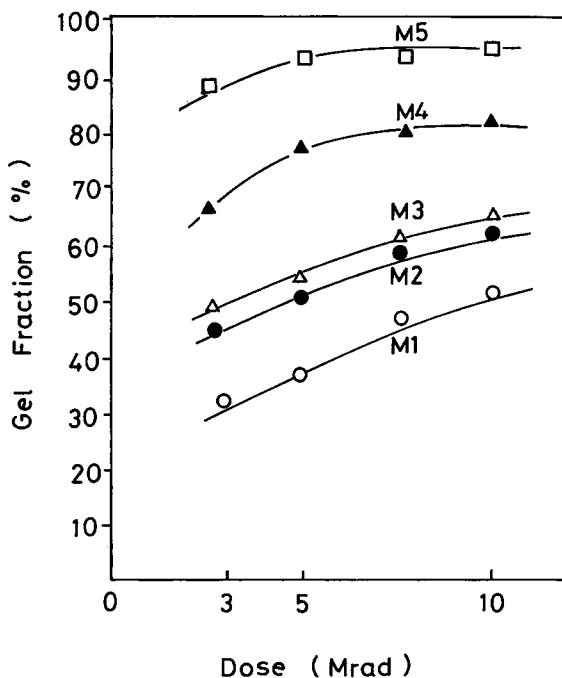
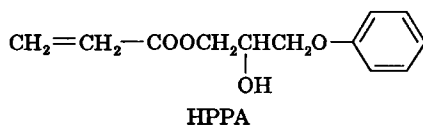


Fig. 4. Gel fraction as function of irradiation dose in the PBA with various content of acryloyl groups-HPPA system. (The ratio of polymer/monomer = 2,  $\bar{M}_w$  of polymer =  $10 \times 10^4$ .)

Mixtures of the mPBA and a monomeric 2-hydroxy-3-phenoxy-propyl acrylate (HPPA) in a 2 : 1 weight ratio were electron-beam-irradiated to afford crosslinked polymeric materials which contain grafts. Peel strength and dead-load strength of the irradiated mPBA-HPPA system are shown in Figures 2 and 3, respectively.



The peel strength depended on both the acryloyl content and the irradiation dose. For a polymer having 1.9 acryloyl groups, the peel strength increased with dose. For the polymers containing 2.5 acryloyl groups or more, the peel strength showed a tendency to decrease with over 5 Mrad irradiation. At 5 Mrad irradiation, the polymers which originally contained 1.9, 2.5, and 48.3 acryloyl groups/polymer showed peel strengths of 600, 470, and 53 g/15 mm, respectively.

The effect of the acryloyl groups on the dead-load strength was similar to that on peel strength. However, for polymers containing up to 2.5 acryloyl groups, the dead-load strength increased with increasing dose. This slight difference between the peel strength and the dead-load strength indicates that a high degree of crosslinking, which is known to contribute to cohesive strength, has more influence on the dead-load than the peel strength.

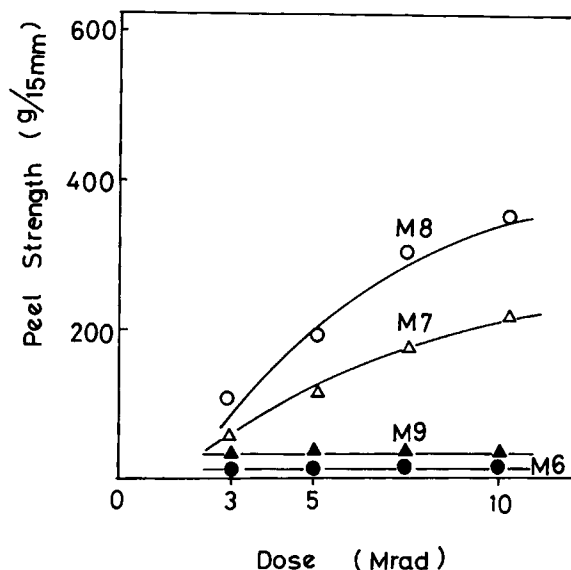


Fig. 5. Peel strength as function of dose in the PBA containing acryloyl groups-HPPA system. ( $\bar{M}_w$  of polymer =  $3 \times 10^4$ .)

As shown in Figure 4, the gel fraction increased as the content of acryloyl groups was raised. Taking into account the relationship between the strength and the dose, shown in Figures 3 and 4, it was revealed that a gel fraction ranging from 40 to 60% results in high peel and dead-load strengths.

Next, similar measurements were performed on lower molecular weight polymers having acryloyl groups. Polymer, having various acryloyl group contents and having  $\bar{M}_w$  of about  $3 \times 10^4$  (see Table III), were compounded with HPPA in the polymer-to-monomer ratio of 2 : 1 and irradiated by EB.

The polymers with acryloyl group contents of 3.1 and 5.6 increased both strengths, as shown in Figures 5 and 6. At 5 Mrad irradiation, the adhesive strength was nearly zero in the absence of acryloyl groups, and cohesive failure was observed. On the other hand, when the polymer had 5.6 acryloyl groups, the peel strength and dead-load strength increased to 200 g/15 mm and 15 min, respectively. Therefore, when the low-molecular-weight polymer is used as the polymer component, higher contents of acryloyl groups are necessary to obtain high adhesive strength. This result suggests that high adhesive strength is acquired by entanglements of polymer chains with considerably higher molecular weight, and so a moderate acryloyl group content is needed. With regard to the irradiated polymer, the gel fraction around 40% affords higher strength, as shown in Figure 7.

As illustrated in Figure 8, the strengths,  $F_a$ ,  $F_b$ , and  $W$  are defined as the adhesive strength between PET film and adhesive, the adhesive strength between steel and adhesive, and the cohesive strength of adhesive, respectively. The overall adhesive strength depends on the balance among these strengths. In general, the failure of adhesive is classified in three types as follows: (1) backing failure, which means 100% transfer of adhesive to steel; (2) cohesive failure; (3) clean release failure, which means that adhesive released from the



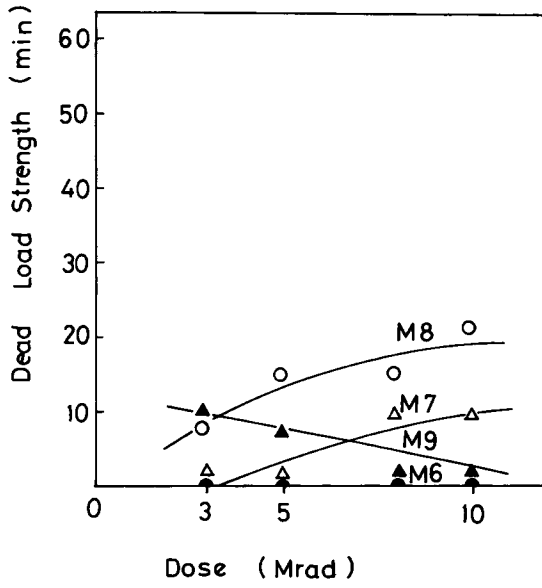


Fig. 6. Dead load strength as function of dose in the PBA containing acryloyl groups-HPPA system. ( $\bar{M}_w$  of polymer =  $3 \times 10^4$ .)

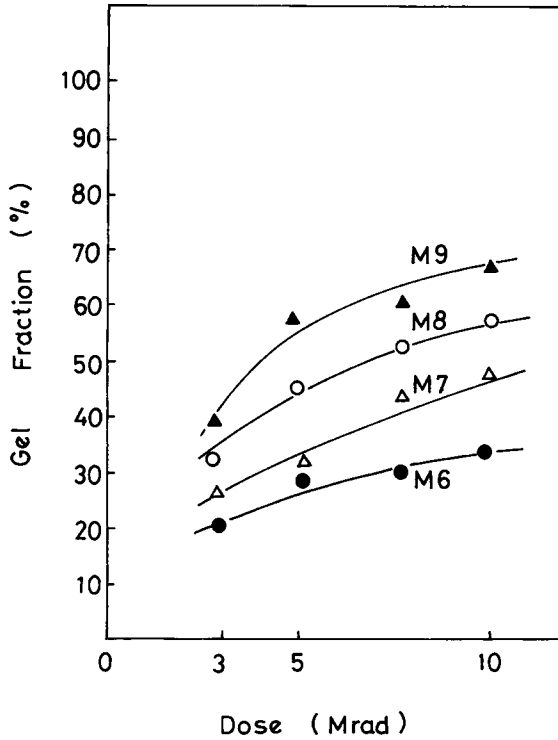


Fig. 7. Gel fraction as function of dose in the PBA with acryloyl groups-HPPA system. ( $\bar{M}_w$  of polymer =  $3 \times 10^4$ .)

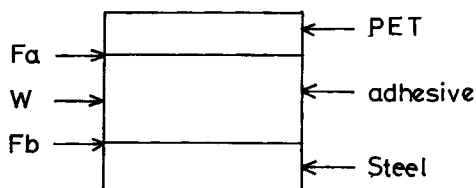


Fig. 8. The typical model of adhesive strength between PET and steel.

steel. The backing failure is caused by low  $F_a$  as compared with  $W$  and  $F_b$ . The other failures (2) and (3) are caused by low  $W$  and  $F_b$ , respectively. In the case of the polymer with  $\bar{M}_w$  of  $10 \times 10^4$ , the main failure was the clean release failure, while in the case of the polymer with low  $\bar{M}_w$  of  $3 \times 10^4$ , cohesive failure mainly occurred. As introduction of acryloyl groups into the polymer caused an increase in  $W$ , the adhesive strength was raised. In the case of the polymer with higher  $\bar{M}_w$  of  $10 \times 10^4$ , which should have higher  $W$ ,  $F_b$  is considered to be relatively lower than the others,  $W$  and  $F_a$ . Thus, clean release occurs.

Ohta and co-workers investigated the adhesive property of acrylic oligomers with  $\bar{M}_w$  of from  $7 \times 10^3$  to  $2 \times 10^4$ .<sup>18</sup> High peel strengths were obtained by the addition of multifunctional mercaptans, though the peel strength of oligomers was low. However, from the viewpoint of pressure-sensitive adhesives, a

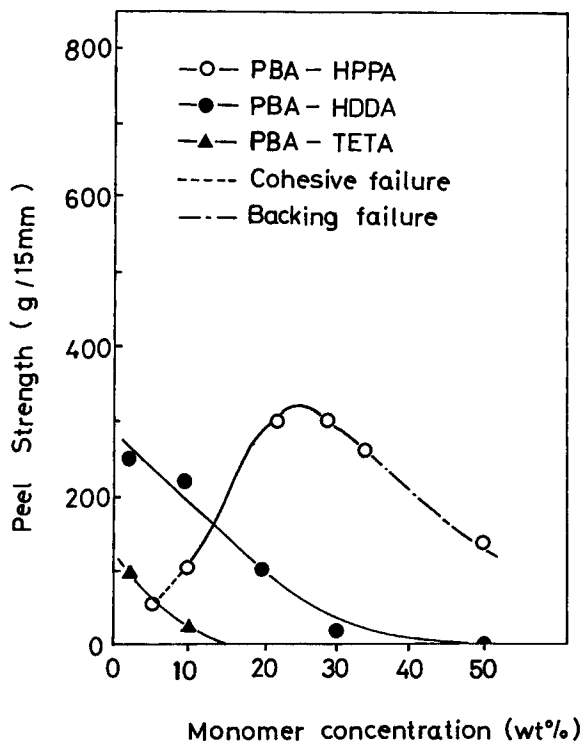


Fig. 9. Peel strength as function of Monomer concentration in the PBA-multifunctional monomer system (5 Mrad irradiation).

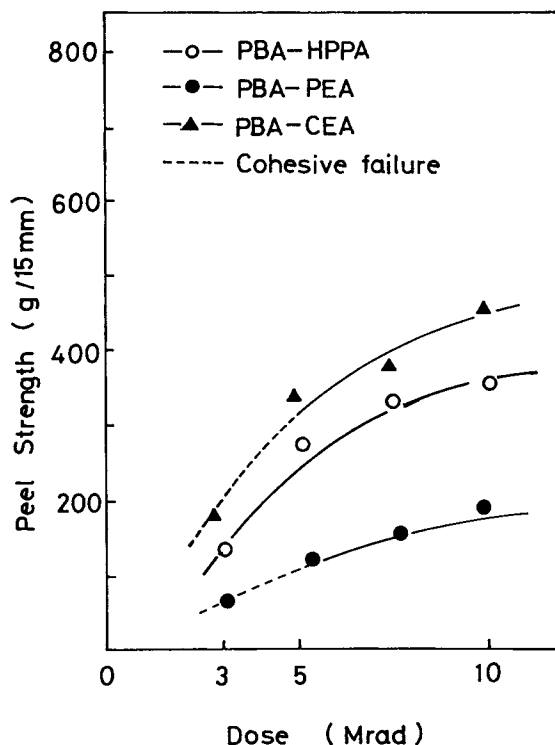


Fig. 10. Peel strength as function of dose in the PBA-monomer system.

sufficient adhesive strength was not acquired without the modification of polymers by acryloyl groups. Therefore, when an adhesive is designed, the main polymer must have  $\bar{M}_w$  of over  $10 \times 10^4$  and a reactive monomer selected so that the cohesive strength is not decreased.

#### Effect of Monomer

In the polymer-monomer system, the selection of monomer was very important. The cohesive strength can be easily increased by the addition of multifunctional monomers, such as HDDA and PETA. However, as shown in Figure 9, the strength of the polymer-multifunctional monomer system could not reach that of the polymer-HPPA system. It is suggested that both polyHPPA and graft polymer, which are generated by EB irradiation, lead to an increase in the adhesive strength. The graft polymer is assumed to play a role as a compatibilizer between the homopolymers of BA and HPPA.

A few other monomers were evaluated in these systems. The peel strengths are shown in Figure 10. The result indicates that surface polarity is an important factor, because the monomers containing carboxyl or hydroxyl groups caused an increase in the peel strength as compared with a nonpolar monomer, PEA.

In conclusion, pressure sensitive adhesives with high adhesive strength were obtained by EB irradiation of the polymer-monomer systems which were composed of PBAs having a few acryloyl groups per polymer molecule, and monomers having a polar group. However, the viscosity of the systems was high,

because monomers with a polar group had high viscosity. It is important to select materials by taking into account a balance between viscosity and adhesive properties for pressure-sensitive adhesive of EB curable polymer-monomer systems.

### References

1. W. Oraby and W. K. Walsh, *J. Appl. Polym. Sci.*, **23**, 3227 (1979).
2. W. Oraby and W. K. Walsh, *J. Appl. Polym. Sci.*, **23**, 3243 (1979).
3. E. Joseph and G. Wilkes, *J. Appl. Polym. Sci.*, **26**, 3355 (1981).
4. W. I. Vroom, D. D. Davis, T. T. Kwei, and T. N. Bowmer, *J. Appl. Polym. Sci.*, **26**, 3669 (1981).
5. G. N. Taylor, M. Y. Hellman, and T. N. Bowmer, *Macromolecules*, **16**, 34 (1983).
6. M. Y. Hellman, W. I. Vroom, and T. N. Bowmer, *J. Appl. Polym. Sci.*, **28**, 2083 (1983).
7. T. N. Bowmer and W. I. Vroom, *J. Appl. Polym. Sci.*, **28**, 3527 (1983).
8. W. A. Salmon and L. D. Loan, *J. Appl. Polym. Sci.*, **16**, 671 (1972).
9. M. Gotoda and Yagi, *Radiat. Phys. Chem.*, **9**, 653 (1972).
10. R. Takiguchi and T. Uryu, *J. Appl. Polym. Sci.*, **30**, 709 (1985).
11. R. Takiguchi and T. Uryu, *J. Appl. Polym. Sci.*, **30**, 3961 (1985).
12. S. Fujita, J. Fujikawa, N. Ueno, and A. Okamoto, *Radiat. Phys. Chem.*, **18**, 864 (1981).
13. K. Pfahl and S. D. Glasscoer, *Radiat. Curing*, **12**(4), 13 (1985).
14. J. Seto, T. Nagai, T. Noguchi, S. Arakawa, A. Shibata, C. Ishimoto, and M. Miyashita, *Radiat. Phys. Chem.*, **25**, 567 (1985).
15. T. M. Santosusso, *Radiat. Phys. Chem.*, **25**, 557 (1985).
16. R. Dowbenko, R. M. Christensen, C. C. Anderson, and R. Maska, *Chem. Tech. Sept.*, 539 (1974).
17. W. C. Perkins, *Radiat. Curing*, **7**(3), 4 (1980).
18. T. Ohta, H. Kanbara, A. Dobashi, and Y. Seki, *Radiat. Phys. Chem.*, **25**, 465 (1985).
19. R. Takiguchi and T. Uryu, *J. Appl. Polym. Sci.*, **31**, 2083 (1986).
20. D. W. Aubrey, G. N. Welding, and T. Wong, *J. Appl. Polym. Sci.*, **31**, 2193 (1969).
21. D. Statas, *Adhesive Age*, **15**, 19 (1972).

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