

11.4 Electron Beam Curing of Dimer Acid-based Urethane Acrylates for Pressure Sensitive Adhesives

Takashi Sasaki*¹, Satoe Takeda*² and Katsutoshi Shiraishi *²

*¹Takasaki Radiation Chemistry Research Establishment,
Japan Atomic Energy Research Institute,
1233 Watanuki-machi, Takasaki, Gunma, 370-12 Japan

*²Research Laboratories, Sanwa Chemical Industries Co., Ltd.,
15 Suzukawa, Ischara, Kanagawa, 259-11 Japan

ABSTRACT

Polyester urethane diacrylate prepolymers prepared from dimer acids (DUA) were cured with low energy electron beams to investigate adhesive properties of cured films. Among various type monomers added, monofunctional methacrylates such as isobornyl methacrylate (IBX-MA) were effective for higher peel strength cured films although the dose-to-cure for the mixtures increased to 100 kGy or more. The increase in the molecular weight of prepolymers resulted in lower curing rates but higher peel strength. Aging tests up to 80 °C for four weeks proved good stability in peel strength of the stored products.

KEYWORDS

Electron beam; curing; urethane acrylate; dimer acids, pressure sensitive adhesives

INTRODUCTION

Dimer acids, derived from unsaturated higher fatty acids, have been well known as raw materials for polyamide resins which have such industrial uses as hardners for epoxy resins and binders for gravure-inks. Due to their chemical structures, hexagonal alicyclic ring with long hydrocarbon chains, the polymers from the dimer acids have lower glass transition temperatures (T_g) and flexibility. In the scope of widely utilizing the dimer acids which are available from natural-based and renewable resources, i.e. vegetable oils, research and development work on converting them into radiation-curable prepolymers have been carried out. The preceding papers from our research group demonstrated the unique properties of cured oligomers based on dimer acids. Such properties are of essential for pressure sensitive adhesives (PSA) which have a wide range of uses. Thus, in order to develop a non-solvent manufacturing system for PSA products, polyester urethane diacrylate prepolymers prepared from dimer acids (DUA) were cured with low energy electron beams to investigate adhesive properties of cured films.

EXPERIMENTAL

Materials

DUA prepolymers used in the present work were prepared as follows. Initially, polyester was prepared by the reaction of dimer acids with a diol. The polyester was then reacted with isophorone diisocyanate (IPDI), and finally the resulting urethane was allowed to react with 2-hydroxyethyl acrylate (HEA) to give an urethane diacrylate.

Irradiation

A sample solution (DUA or DUA/monomer mixture) was coated on PET film with a baker type applicator at about 25 μm thickness. The coated films were irradiated to be cured using a 60 cm wide Curetron (NHV) at an acceleration voltage of 250kV and a beam current of 30 mA in nitrogen atmosphere.

Measurements and Testing

Adhesive properties evaluated were 180° peel strength, ball tack and holding power. The 180° peel strength was evaluated on strips of 25 mm width pasted onto a stainless steel panel (SUS 304) at a crosshead speed of 300 mm/min by using a Strograph-W2 (Toyo Seiki Co., Ltd.). The ball tack was measured by the J. Dow method at 30° slope. Holding power was evaluated for a sample adhered onto a SUS 304 panel with an area of 25 mm x 25 mm at 40 °C under a load of 1kg. Gel fraction was measured by Soxhlet's extraction with boiling acetone. Molecular weight was determined by using a Shodex DS-4 (Showa Denko Co., Ltd.). The Tg was measured by using a DSC/5200 (Seiko Instruments Inc.).

RESULTS AND DISCUSSION

Monomer Selection

The adhesive properties of DUA mixed with various monomers are shown in Table 1. The DUA oligomer used here was prepared from dimer acid, 1,6-hexanediol, IPDI, and HEA. It can be seen that DUA without monomer can be cured at comparatively low dose and that the

Table 1 Adhesive properties of the oligomer mixed with monomers

Monomer* ¹	Dose (kGy)	Peel strength* ² (g/25mm)	Ball tack (No.)	Holding power* ³ (hr)	% Gel (%)
None	30	7	5	> 24	90
	50	6	5	> 24	92
THF-A	50	25	4	> 24	91
IBX-A	50	540	2	> 24	83
L-A	50	7	5	> 24	79
ID-A	50	5	5	> 24	80
EDCP-A	50	40	6	> 24	79
DCP-DA	20	3	<2	> 24	88
NP-DA	20	4	<2	> 24	89
THF-MA	100	350	10	> 24	75
IBX-MA	100	420	7	> 24	80
L-MA	100	295	16	> 24	78
ID-MA	100	400	13	> 24	74
EDCP-MA	100	100	7	> 24	86

*1 DUA/A = 70/30 DUA/DA = 80/20 DUA/MA = 80/20

A: monoacrylate DA: diacrylate MA: monomethacrylate

THF: tetrahydrofurfuryl IBX: isobornyl L: lauryl ID: isodecyl

EDCP: ethylene oxide modified dicyclopentenyl DCP: dicyclopentenyl

NP: neopentyl-glycol

*2 on stainless steel(SUS 304)

*3 at 40°C, 1kg load

cured film has low peel strength. As for DUA /monomer mixed systems, it seems that the structure of monomer influences the adhesive properties and the curing speed. DUA with mono-acrylate is more reactive than DUA with mono-methacrylate, while the result is reverse as for the peel strength. DUA with di-acrylate is much more reactive than those with others, but the cured film has low peel strength and tack. As for the structure of mono-acrylate monomers having cyclic structure (IBXA, THFA and IDA) showed higher peel strength than monomers with linear structure (LA and IDA). Among these monomers IBXA gave the highest peel strength. However, IBXA is unfavorable for practical use because of the strong smell and toxicity. Therefore, isobornyl methacrylate (IBXMA), having moderate smell and toxicity, was selected for diluent of DUA in the following investigations.

Effect of Molecular Weight of DUA

The relationship between molecular weight of DUA and the adhesive properties of the cured oligomers are shown in Table 2. These oligomers have the same components (dimer acid, 1,6-hexanediol, IPDI, and HEA) and are mixed with 20% of IBXMA. Table 2 clearly shows the tendency that the oligomer with lower molecular weight is more reactive and the cured film has lower peel strength than the oligomer with higher molecular weight. Therefore, in the design of the adhesive, the oligomer with moderate molecular weight should be chosen in consideration of the use.

Table 2 Relationship between molecular weight and adhesive properties

Molecular weight of DUA	6,100	17,500	21,200	28,600
Dose (kGy)	10	50	100	150
Peel strength (g/25mm)* ¹	3	70	600	990
Ball tack (No.)	< 2	< 2	3	11
Holding power (hr)* ²	>24	>24	>24	>24
Gel fraction (%)	73	88	89	87

*1 stainless steel(SUS 304)

*2 at 40 °C, 1kg load

Properties of DUA Based on Various Diols

Table 3 shows the adhesive properties of cured DUA prepolymers prepared from dimer acids and various diols. These oligomers except the one based on PPG are mixed with 20% of IBXMA. The oligomer based on PPG mixed with 20% of IBXMA was not curable even at the dose of 200 kGy. From Table 3, it is found that oligomer based on various diols showed moderate peel strength and adequate holding power. The oligomer based on PPG seems to be suitable for removable type adhesives.

Table 3 Properties of DUA based on various diols

Diol	Molecular Weight (Mw)	Dose (kGy)	Peel strength* ¹ (g/25mm)	Ball tack (No.)	Holding power* ² (hr)	% Gel (%)
diethylene glycol	16,300	100	480	10	>24	65
1,5-pentanediol	20,700	100	550	13	>24	78
1,6-hexanediol	21,200	100	600	3	>24	89
polypropylene glycol	26,500	20	135	8	>24	85

*1 stainless steel(SUS 304)

*2 at 40 °C, 1kg load

Tg of the Cured DUA

Fig. 1 shows the DSC thermograms of cured DUA and DUA/IBXMA mixture. The Tg values determined from the thermograms are below -50°C . It is rather surprising that the latter has such a low Tg in spite of high Tg (180°C) of poly-IBXMA. The high peel strength of the cured DUA/IBXMA mixture is probably due to its low Tg value.

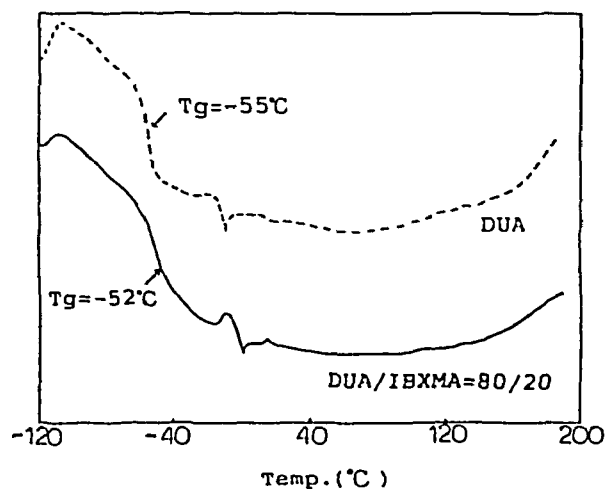


Fig.1 Tg of the cured DUA

CONCLUSION

The present work demonstrated that the EB cured DUA formulations showed high cohesion strength (holding power) and a wide range of peel strength depending upon the chemical structure and molecular weight of the DUA and diluent monomers used. It should also be noted that the products had excellent thermal stability. Thus it can be concluded that EB curing of DUA is one of most potential candidates for non-solvent processing of PSA products.

REFERENCES

- 1) A.Shakri and T. Sasaki, Proceedings of CRCA '88, pp.202-206
- 2) K Zaman and T.Sasaki, Proceeding of Radtech Asia '91, pp.359-364