Polymer Bulletin 27, 213–220 (1991)

Polymer Bulletin

Effect of monofunctional diluents on the mechanical properties of electron beam cured films obtained from urethane prepolymers

Kohichiro Kawate[1] **and Takashi Sasaki**[2]

[1]Sumitomo 3M Corporate Development Laboratory, 8-8, Minami-hashimoto 3-chome, Sagamihara, Kanagawa 229, Japan
[2]Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, 1233 Watanuki-machi, Takasaki, Gunma, 370-12 Japan

Summary

Tensile properties of EB-cured films of urethane acrylates and reactive diluent mixtures were investigated. Experimental data for urethane acrylate/monofunctional diluent systems were found to cover a wide range of tensile properties compared to urethane acrylate/multifunctional diluent systems. In the plot of tensile properties vs. Tg of homopolymers of monofunctional diluents, the elongation curves showed a maximum near ambient temperature and the tensile strength increased rapidly above this temperature.

Introduction

Acrylated urethane oligomers have been widely used as coating and binder resins owing to their diverse variety of structures and properties (1). Since such prepolymers are generally viscous or almost solid, reactive diluents are usually used to reduce the viscosity. A reactive diluent may influence the cure rate and toxicological properties of the solution, and mechanical and adhesion properties of cured films.

Several authors (1-5) have investigated the effect of reactive diluents on the mechanical properties of cured films. Multifunctional diluents generally increase the tensile strength of the film while elongation is decreased due to increase in the crosslinking density of cured film (1,4,5). Monofunctional diluents have been generaly believed to reduce the tensile strength and enhanced the elongation of the acrylated urethane polymer (1). However, N-Vinyl pyrolidone(NVP) has been found to enhance both tensile strength and elongation by adding to urethane acrylates (1-4). This finding is thought to be rather exceptional example. Thus, the effect of monofunctional diluents on the mechanical properties has not been totally clear untill now.

The present report describes the mechanical properties of EB-cured films obtained from mixtures of urethane acrylate oligomers and monofunctional diluents.

Experimental

Materials

Commerically available urethane acrylates, UX-4101 (Nippon Kayaku Co., Ltd.) and UV-7700B(Nippon Synthetic Chemical Industry Co., Ltd.) were used. These urethane acrylates are based on aliphatic diisocyanate and have one acrylate group at each end. The characteristics of these oligomers are listed in Table 1. UX4101 and UV7700B yield flexible and semi-flexible films after EB irradiation, respectively.

Reactive diluents used in this study are given in Table 2. The glass transition temperatures of the diluent homopolymers shown in Table 2 are literature values (6) except for the one for poly(DPA) which was referred to the supplier's (Hitachi Chemical Co., Ltd.) datum using DSC.

Sample Preparation and Irradiation

The resin formulations were prepared by mixing each of the urethane acrylates with diluents at 40 °C. Pure UX4101 was heated at 80 °C for 20 min to reduce the viscosity before preparation. The resin samples for irradiation were prepared by drawing the resin/PET (thickness: 50 μm, width: 15 cm) sandwich through a given clearance of a knife coater head. The sandwich was irradiated with 300 kV electron beam generated from a 60 cm wide multi-linear filament type accelerator (Curetron, Nissin-High Voltage Co., Ltd.) at a beam current of 30 mA. The conveyor speed was 15 m/min and the dose per pass was 50 kGy. Each sample was passed under the beam, once on each side. The thickness of the sample film was kept in the range of 300-400 μm.

Tensile Measurements

Tensile strength and elongation at break were measured by using a Strograph-R1 (Toyo Seiki Co.,Ltd.). The tension speed used was 10 mm/min. Young's modulus was determined from the stress-strain curve measured. The results given in the following section are the mean of five readings. The measurements were carried out within 24 h after irradiation at room temperature.

Results and Discussion

Data obtained from the experiments are listed in Table 3. Fig.1 shows the plot of elongation vs. tensile strength obtained for UX4101/diluents. It can be seen from Fig.1 that the formulations of UX4101/monofunctional diluents cover a wide range of tensile properties while the formulations of UX4101/multifunctional diluents have a narrow range of tensile properties. It should be noted that some monofunctional diluents enhanced both tensile strength and elongation.

Table 1 Characteristics of urethane acrylates

	UX4101	UV7700B
Viscosity at[a] 60°C (poise)	300-400	20-50
Mn[b]	2700	2500
Mw[b]	5300	9600
Tg of cured films (°C)	15[c]	45[a]

a) reported by the suppliers
b) measured with GPC
c) measured with dynamic mechanical spectrometer

Table 2 List of monomers

Abbreviation	Name	Tg of polymer (°C)
Monofunctional		
IOA	Isooctyl acrylate	-65
nBA	n-Butyl acrylate	-54
EHA	2-Ethylhexyl acrylate	-50 (-85)[a]
MTA	2-Methoxyethyl acrylate	-50
EA	Ethyl acrylate	-24
BzA	Benzyl acrylate	6
MA	Methyl acrylate	10
CHA	Cyclohexyl acrylate	19
VAc	Vinyl acetate	32
tBA	t-Butyl acrylate	43
IBA	Isoboronyl acrylate	94
AA	Acrylic acid	106
DPA	Dicycopentanyl acrylate	120
NVP	N-Vinyl pyrolidone	175
Multifunctional		
HDDA	1,6-hexanediol diacrylate	
PNGD	Propxylated neopentyl glycol diacrylate	
TPGD	Tripropyleneglycol diacrylate	
NGTD	Neopentylglycolated trimethylolpropane diacrylate	
EBAD	Ethoxylated bisphenol A diacrylate	
PTPT	Propoxylated trimethylolpropane triacrylate	

a) from Ref 1)

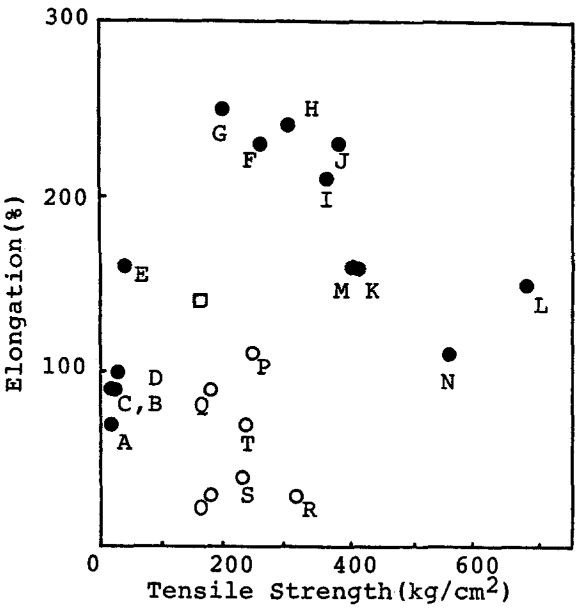

Fig.1 :Tensile properties of electron beam cured films. □: neat UX4101, ● : UX4101/monofunctional monomer, o : UX4101/multifunctional monomer.

In order to understand the effect of monofunctional diluents on tensile properties of the cured films, the tensile strength and elongation for the formulations of UX4101/monofunctional diluents are plotted against the Tg for the diluent homopolymers as shown in Fig.2. From the plot, it can be seen that the tensile properties are dominated by the Tg of the diluent homopolymers. The elongation curve shows a maximum at a Tg near room temperature while the tensile strength seems to increase sharply above this temperature range with increasing Tg. Similar behaviour for tensile properties vs. Tg were obtained for UV7700B/monofunctional diluents as shown in Fig.3.

Next, mixed diluents were used instead of a single diluent in order to vary the glass transition temperature of the diluent homopolymers. A mixture of 2-ethylhexyl acrylate (EHA) and dicyclopentanyl acrylate (DPA) was used in this study because the Tg of poly(EHA) (-85 °C) is much lower than the Tg of poly(DPA) (120 °C). In Fig.4, the tensile strength and elongation observed for the formulation of UX4101/mixed diluents are plotted against the weight fraction of DPA in the mixed diluent. The curves of tensile strength and elongation vs. Tg for UX4101/mixed diluents are very similar to those shown in Fig.2. The Tg of the copolymer of EHA and DPA at the maximum position in the elongation curve was evaluated to be 20-45 °C by using the Fox's equation (7). These observations support the suggestion that the Tg of the diluent homopolymer dominates the tensile properties of EB cured films.

In general, monofunctional diluents will reduce the crosslinking density and give a looser structure by adding to a difunctional oligomer. Therefore, an increase in elongation can be attributed to a decrease in crosslinking density. However, the characteristic behaviour shown in Fig.2-4 cannot be fully explained by the formation of the looser structure above. These phenomena should be explained from a different point of view.

Table 3 Tensile properties of electron beam cured films

Components	Tensile Strength (kg/cm^2)	Elongation (%)	Young Modulus (kg/cm^2)
UX4101	170	140	20
A. UX4101/IOA=60/40	20	70	30
B. UX4101/nBA=60/40	20	90	30
C. UX4101/EHA=60/40	20	90	30
D. UX4101/MTA=60/40	30	100	30
E. UX4101/EA =60/40	40	160	30
F. UX4101/BzA=60/40	260	230	40
G. UX4101/MA =60/40	200	250	40
H. UX4101/CHA=60/40	300	240	70
I. UX4101/VAc=60/40	360	210	40
J. UX4101/tBA=60/40	380	230	300
K. UX4101/IBA=60/40	410	160	5700
L. UX4101/AA =60/40	680	150	12400
M. UX4101/DPA=60/40	400	160	4600
N. UX4101/NVP=60/40	560	110	12000
O. UX4101/HDDA=70/30	180	30	1500
P. UX4101/PNGD=80/20	250	110	170
Q. UX4101/TPGD=80/20	180	90	230
R. UX4101/NGTD=70/30	320	30	9100
S. UX4101/EBAD=60/40	240	40	5100
T. UX4101/PTPT=70/30	240	70	270
UV7700B	150	60	230
a. UV7700B/EHA=60/40	20	40	20
b. UV7700B/MTA=60/40	30	40	20
c. UV7700B/EA =60/40	60	80	20
d. UV7700B/MA =60/40	130	130	110
e. UV7700B/tBA=60/40	320	110	3800
f. UV7700B/IBA=60/40	300	60	8500
g. UV7700B/DPA=60/40	310	50	12400

It is well known that temperature has a large effect on all the strain-stress properties (8). When the temperature is raised from below to above Tg, the elongation of a single polymer sharply increases near Tg and decreases again at higher temperature. On the other hand, the tensile strength generally decreases with an increase in temperature. The Young's modulus decreases sharply near Tg as temperature is increased. The effect of temperature on mechanical properties for any polymer can be better demonstrated if (T-Tg) is used as the variable rather than the temperature. Increasing ambient temperature gives a similar effect to lowering the Tg by the addition of plasticizer (8). The present observation can be explained well from this scheme. The Tg of cured films would be influenced by that of the diluent homopolymers. With an increase in the Tg of the diluent homopolymers, the Tg of the cured films increase and the tensile strength and the elongation are enhanced. The observation of a maximum in elongation as shown in Fig.2-4 suggests that the Tg of the cured films are near room temperature. The Tg of sample H in Table 3 was determined to be 23 °C by using dynamic mechanical measurements.

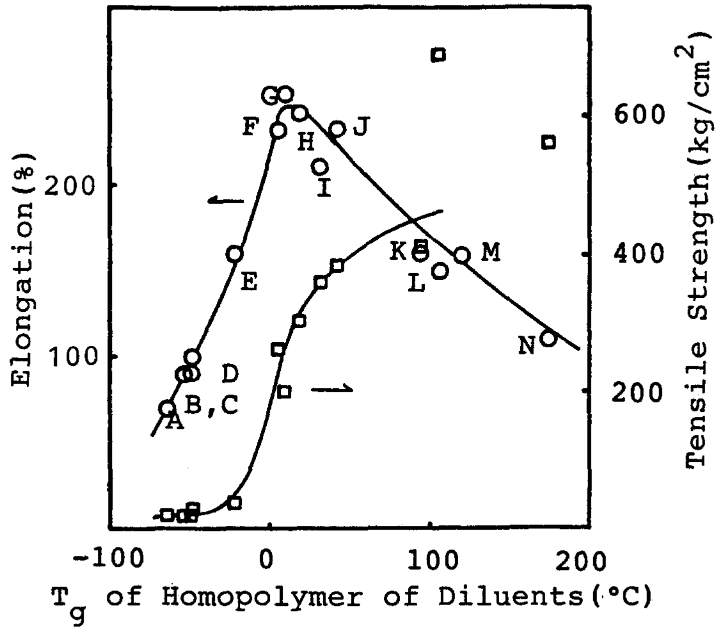

Fig.2 : Tensile properties of UX4101/monofunctional diluent sysytems are plotted against the Tg of the diluenht homopolymers.

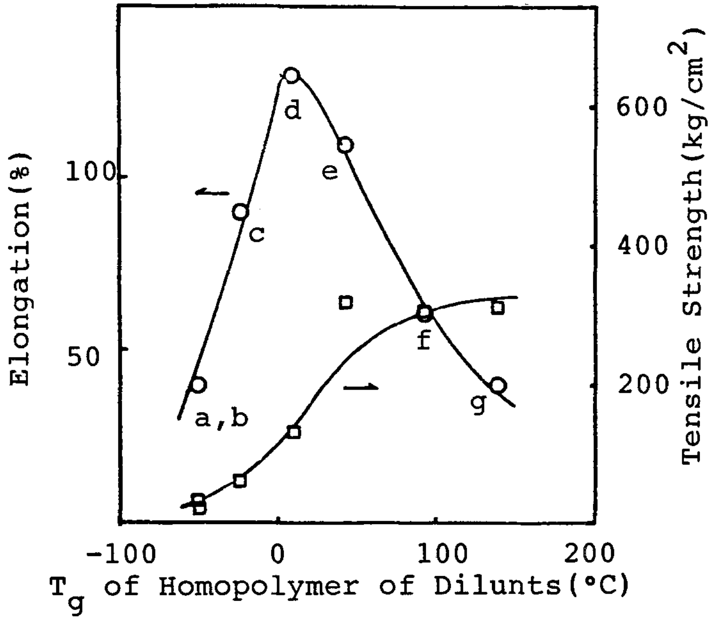

Fig.3 : Tensile properties of UV7700B/monofunctional diluent systems are plotted against the Tg of the diluent homopolymers.

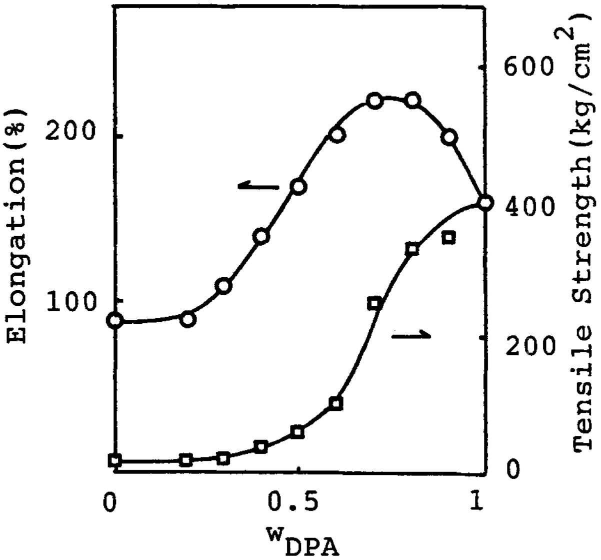

Fig.4 : Tensile properties of UX4101/mixed diluents of EHA + DPA are plotted against the weight fraction of DPA W_{DPA} in the mixed diluent.

Table 3 clearly shows that the tensile strength and Young's modulus of cured films containing acrylic acid and N-vinyl pyrolidone are extremely large. This could be attributed to the differences in polymer structure from those of other acrylate copolymers due to the differences in copolymerization for NVP and hydrogen-bond formation for AA.

The formulations L, N and g in Table 3 all yielded a high Young's modulus. When these films were strained beyond their elastic limit, permanent deformation occurred. However, it was found observed that the deformed films lost their deformation spontaneously and even the folds disappeared on heating. This observed behaviour can be regarded as a shape memorizing property. Shape memorizing properties were not observed for the formulations of UX4101/multifunctional diluents. In Table 3, the formulation R and S yielded lower Young's modulus than those of L, N and g but these films were broken when strained beyond their elastic limit.

Conclusion

The present study has shown that those formulations containing monofunctional diluents cover a wide range of mechanical properties from very strong to very elastic films, with some having superior shape memorizing properties.

Acknowledgement

The authors wish to thank Mr. S. Tanno at Sumitomo 3M Limited and his group for the GPC data and Mr. N. Toriumi at Sumitomo 3M Limited for the dynamic mechanical data.

References

1. Papas S.P. Ed.(1985) UV Curing. Science and Technology. Vo 2, Technology Marketing Corp., Norwalk, Conn.
2. Oraby W. Walsh W.K.(1979)J. Appl. Polymer Sci.23:3227
3. Oraby W. Walsh W.K.(1979)J. Appl. Polymer Sci.23:3243
4. Kobayashi K., Hwang K.K.S., Foley S.K., Yarusso D.J. Cooper S.L.(1982)J. Mater. Sci., 17:1447
5. Joseoh E. Wilkes G.(1981)J. Appl. Polymer Sci.,26:3355
6. Brandrup J. Immegut E.H. Ed.(1985)Polymer Handbook, 3rd Ed., Wiley, New York, NY.
7. Fox T.G.(1956)Bull. Am. Phys. Soc., 1:123
8. Nielsen L.E.(1974)Mechanical Properties of Polymer and Composites, Marcell Dekker, New York, Chapter 5
9. Nielsen L.E. Buchdahl R. Levreault R.(1950)0 J. Appl. Phys., 21:607

Accepted July 29, 1991 S