Properties of UV-Curable Polyurethane Acrylates for Primary Optical Fiber Coating

HAN DO KIM,* SEUNG GU KANG,[1] and CHANG SIK HA[2]

[1]Department of Textile Engineering, Pusan National University, Pusan 609-735, South Korea
[2]Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, South Korea

SYNOPSIS

Studies have been made on the effects of the chemical structure of reactive urethane acrylate prepolymers and diluents (reactive monomers) and overall composition of the prepolymer/ diluent on the properties of the UV-curable polyurethane acrylates for primary optical fiber coating. We prepared several urethane acrylate prepolymers from two different iso-cyanates, 4,4'-dicyclohexylmethane diisocyanate (HMDI) or isophorone diisocyanate (IPDI), and two different polyols, polybutadiene diol (PBD) or polypropylene oxide diol (PPG), and 2-hydroxyethyl acrylate (HEA) with dibutyl tin dilaurate as a photoinitiator. UV-curable coating materials were formulated from the prepolymers and 2,2-dimethyl 2-phenyl acetophenone as a photoinitiator with one of four different diluents such as 1-vinyl 2-pyrrolidone (VP), lauryl methacrylate (LMA), acrylic acid 2-ethyl hexyl ester (AEHE), and acrylic acid n-butyl ester (ABE). It was found that AEHE is the desirable diluent in the formulation of the primary fiber-coating material. The desirable composition of PBD, when mixed PBD/PPG diols are used, should be about 50 wt % for optimum formulation. Most of the urethane acrylate prepolymers prepared in this study could be applied in the formulation of primary optical fiber coating and exhibited good properties of buffer functions, including low glass transition temperature, low modulus even at low temperature, say, below −40°C, high refractive index, and low viscosity. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The use of optical fibers for communication purposes has attracted much interest since the late 1960s. Even though significant progress has been made to activate the limitless potential for the lightwave communications, its inherent characteristics such as brittleness and optical loss limit the direct outdoor use of the fibers unless precautions are taken. It is well known that the loss decreases when a protective coating is applied to the fiber. The coating protects the fiber against microbending loss and the transmittance of external forces to the fiber. Twofold coating is applied in the optical fiber industries: The primary or buffer coating should have good flexibility with low modulus to prevent microbending,[1,2] while the secondary coating should have high modulus and chemical resistance so that external stresses are not transmitted to the fiber. Table I summarizes the general requirements of each coating.

As shown in Table 1, the primary coating should maintain low modulus even at low temperature (say, −40°C) and, at the same time, have a larger refractive index than 1.46 to reduce a cladding mode loss, especially in the multimode step index fiber. Among the several attempts to coat the optical fiber, the application of UV-curable coating has been widely investigated because of its fast cure speed and energy-saving characteristics in spite of its relatively high cost over thermal-cured coating.

In this study, we concentrated on the UV-curable primary coating materials for the fibers. The UV-curable coating materials are formulated with the three basic components including prepolymer, diluent, and photoinitiator. The properties of the coating material like modulus, refractive index, viscosity,

Table I   General Requirements of UV-curable Resin for Optical Fiber

Primary Coating

　　Low modulus over the range of operating
　　　(< 10 MPa)
　　Good adhesion to the glass
　　High index of refraction (> 1.46)
　　Long-term durability
　　Low hydrogen generation

Secondary coating

　　High modulus to resist external lateral forces
　　　(> 1 GPa)
　　Low coefficient of friction
　　Excellent resistance to environmental
　　　factors
　　Low water absorption
　　Low hydrogen generation

Processability

　　Rapid cure speed (5 m/s)
　　Optimum viscosity (< 100 poise)

and cure speed are dependent on the type of prepolymer and diluent and the overall composition of the formulation.

Urethane acrylates have been intensively studied for optical fiber coating. Naruse and Sagawara[3] reported on the effect of modulus of primary coating on the loss due to microbending. Bishop[4] developed a UV-cured coating material based on polypropylene diacrylate (MW 1000) and polyoxybutylene diacrylate (MW 1150) and reported the coating material had low modulus and high refractive index. Fluoroepoxy acrylate and fluoroepoxy methacrylate were also used for UV-curable coating by Nakamura et al.[5]

Kimura and Yamakawa[6,7] studied the effect of diluent structure and concentration on the UV-curable coating at a given prepolymer concentration and reported that the formulation from the polybutadiene diol (PBD)-based prepolymer was very viscose and not to be processable for coating. In this vein, we used polypropylene glycol (PPG) or a mixture of PPG and PBD with various concentrations as well as PBD alone to prepare the urethane prepolymers. We investigated the effects of the types and concentrations of the polyols on the properties of the final coating film.

For this work, we selected urethane acrylates as the prepolymer because these materials have the potential to combine the high abrasion resistance, toughness, tear strength,[8,9] and good low-temperature properties of polyurethanes with the superior optical properties and weatherability of polyacrylates. The reactive mixture of urethane oligomer tipped with acrylic functionality was combined with reactive diluents (vinyl monomer), which were added to reduce the viscosity of the liquid precursor mixture to provide better processibility. In the present article, the effect of oligomer type, reactive diluent type, and concentration and overall composition of the prepolymer/diluent on the properties of the UV-curable polyurethane acrylate for primary optical fiber coating were investigated.

EXPERIMENTAL

Materials

4,4'-Dicyclohexylmethane diisocyanate (HMDI, Aldrich Chemical) and isophorone diisocyanate (IPDI, Aldrich Chemical) were used as received. 1,4-Polybutane diol (PBD) (MW 3,000, Aldrich Chemical) and polypropylene oxide diol (PPG) (MW 2,000, Aldrich Chemical) were degassed at 80°C for 6 h under vacuum. The 2-hydroxyethyl acrylate (HEA, Aldrich Chemical) and the diluents (Aldrich or Wako Chemical) listed in Table II were kept dry with a molecular sieve (4 Å) before use for 1 week. Dibutyl tin dilaurate (Fluka Chemical) and 2,2-dimethoxy-2-phenyl acetophenone (DMPAP, Aldrich Chemical) were used without further purification.

Table II   Chemical Structure of Diluents for the Primary Coating Material

Diluent	Structure
Acrylic acid 2-ethyl hexyl ester (AEHE)	$CH_2{=}CH$ $\|$ $COOC_8H_{17}$
Acrylic acid n-butyl ester (ABE)	$CH_2{=}CH$ $\|$ $COO(CH_2)_3CH_3$
Lauryl methacrylate (LMA)	CH_3 $\|$ $CH_2{=}C$ $\|$ $COO(CH_2)_{11}CH_3$
1-Vinyl, 2-pyrrolidone (VP)	$CH_2{=}CH$ $\|$ N—O

Syntheses of Urethane Acrylate Prepolymers

HMDI- (or IPDI)-based urethane acrylate prepolymers were synthesized by adding an equimolar amount of dehydrated HEA dropwise to HMDI or IPDI under a nitrogen atmosphere. The reaction temperature was kept below 45°C to avoid thermal polymerization of vinyl groups. When the temperature of the HMDI (or IPDI)/HEA reaction mixture started to drop, a stoichiometric quantity of dehydrated polyol was added along with dibutyl tin dilaurate catalyst (3 wt %). The mixture was agitated for 2 h and heated to 70°C to complete the reaction.

Then, the UV-curable liquid mixtures were formulated from the above viscous oligomers by adding the 3 wt % of photoinitiator DMPAP and the required amount of proprietary diluent listed in Table II prior to curing. The air bubbles entrapped during mixing were removed by applying vacuum at 30°C for 30 min and kept under vacuum at 60°C for 3 h.

UV Curing

The final UV-cured urethane acrylates films were prepared by casting the above-formulated product onto a glass plate at room temperature and cured using a medium-pressure mercury lamp (80 W/cm). Radiation curing has been carried out with the UV light of 365 nm of main wavelength. The thickness of the cast film was about 300 μm.

Measurements

IR Spectra

IR spectra of urethane acrylate prepolymers before and after UV irradiation were taken to compare degree of cure on a Fourier transform infrared spectra (Perkin-Elmer 1330) using thin films cast on KBr pellet.

Gel Content

The gel contents of the cured film samples was determined by Soxhlet extraction using toluene for 24 h. The insoluble materials were dried under vacuum for about 2 days and weighed to determine the gel contents. The gel content of the cured film samples was determined from the difference in weight before and after the extraction experiment as follows:

$$\text{gel content (\%)} = w/w_0 \times 100$$

where w_0 and w are sample weights before and after extraction, respectively. Several runs were made for each sample, and average values were taken.

Viscosity

Viscosity of the UV-curable liquid mixtures before curing was measured with Brookfield viscometer (model LVTDV-II) over the temperature range of 50–70°C.

Refractive Index

The refractive index of cured film samples (thickness 0.5–1 cm) was measured by the traveling microscope (Atag Co.). The refractive index, n, was determined from the positions in the microscope as follows:

$$n = \frac{(t_3 - t_1)}{(t_3 - t_1) - (t_2 - t_1)} = \frac{t}{t - e}$$

where t_1 is the position of reference surface and t_2 and t_3 are the position of top of a sample and the vertical image position of top reference surface, respectively. t is the difference between t_3 and t_1 and e is the difference between t_2 and t_1.

Dynamic Mechanical Measurements

The dynamic mechanical properties were obtained at 35 Hz using Rheovibron DDV-II (Toyo Baldwin Co.) with a heating rate of 2°C/min over a temperature range of −80 to 80°C. Film samples of about 0.3 mm thick $\times$ 1 cm wide $\times$ 3 cm long were prepared.

RESULTS AND DISCUSSION

Curing Evaluation and General Properties

The composition and the properties of coating material are summarized in Table III. Details of the results will be discussed in each proper section.

We tested preliminarily many other urethane acrylate systems but reported only the formulations having suitable properties for application as primary coating for optical fiber as stated in Table I. For instance, we studied urethane prepolymers from different isocyanates like toluene diisocyante (TDI) or 4,4′-diphenylmethane diisocyanate (MDI), but we knew that only HMDI and, at most, IPDI could be candidates as suitable isocyanates for the formulation of the primary optical fiber coating, since

Table III Composition, T_g, Viscosity, and Refractive Index of Primary Coating Materials Prepared for Optical Fiber

Composition of Prepolymer Isocyanate/hydroxy acrylate/polyol	Diluent (wt %)	Refractive Index of Polymer Prepared	T_g (°C)	η (cps) at 70°C
HMDI/HEA/PPG	0	1.48	−46	
HMDI/HEA/PPG	AEHE (9)	1.46	−44	615
HMDI/HEA/PPG	AEHE (17)	1.43	−48	390
HMDI/HEA/PPG	AEHE (23)	1.38	−49	185
HMDI/HEA/PPG	LMA (9)		−49	
HMDI/HEA/PPG	VP (9)		−48	
HMDI/HEA/PPG	ABE (17)		−48	
HMDI/HEA/PBD	AEHE (23)	1.52		
HMDI/HEA/PBD			−70	
TPDI/HEA/PPG	0	1.47	−51	
HMDI/HEA/PBD(80%)/PPG(20%)	0		−56	
HMDI/HEA/PBD(80%)/PPG(20%)	AEHE (23)	1.50	−59	
HMDI/HEA/PBD(50%)/PPG(50%)	0		−67	
HMDI/HEA/PBD(50%)/PPG(50%)	AEHE (23)	1.48	−50	556
HMDI/HEA/PBD(20%)/PPG(80%)	0		−50	
HMDI/HEA/PBD(10%)/PPG(90%)	AEHE (17)			230
HMDI/HEA/PBD(10%)/PPG(90%)	AEHE (23)			171
HMDI/HEA/PBD(10%)/PPG(90%)	AEHE (29)			109

T_g: Glass transition temperature determined by Rheovibron; viscosity at 70°C.

the urethane prepolymers started from the two isocyanates showed generally good properties to meet the requirements mentioned in Table I. Note, however, that HMDI is used to prepare most of the urethane acrylates in this study, unless specially indicated.

The curing of the urethane acrylate prepolymers was analyzed by FTIR. Figure 1 shows a typical IR spectrum of HMDI/HEA/PPG urethane prepolymer before and after UV irradiation for 1 s. The urethane acrylate prepolymer was identified by the characteristic peaks around 2270 cm^{-1} (N=C=O)

and 1720 cm^{-1} (C=O). The urethane acrylate has a C=C absorption band at 1635 cm^{-1} before UV irradiation, but the band was no longer detectable after irradiation. The characteristic C=C absorption of urethane acrylate at 1635 cm^{-1} was used to determine the extent of photopolymerization. The N=C=O stretching band near 2270 cm^{-1} was used to monitor the extent of the reaction between isocyanate and the hydroxy group. The result in Figure 1 indicates that radiation curing and the isocynate reaction had been performed. The structure of the typical acrylated urethane oligomer is shown below:
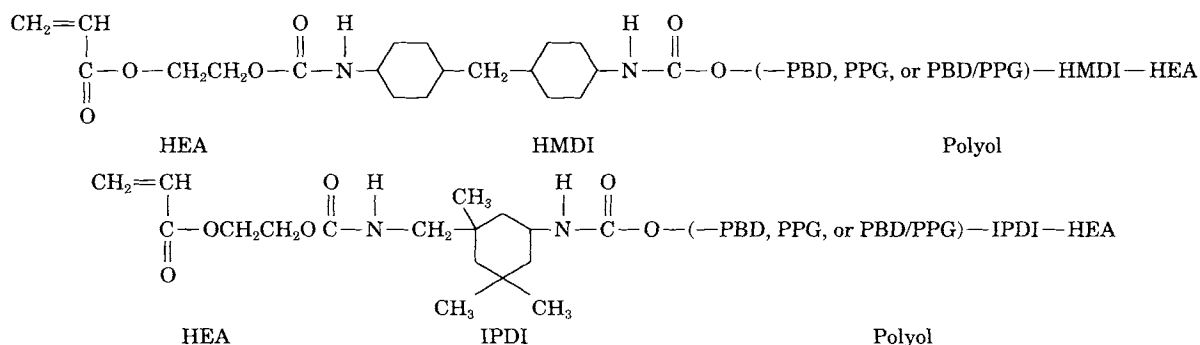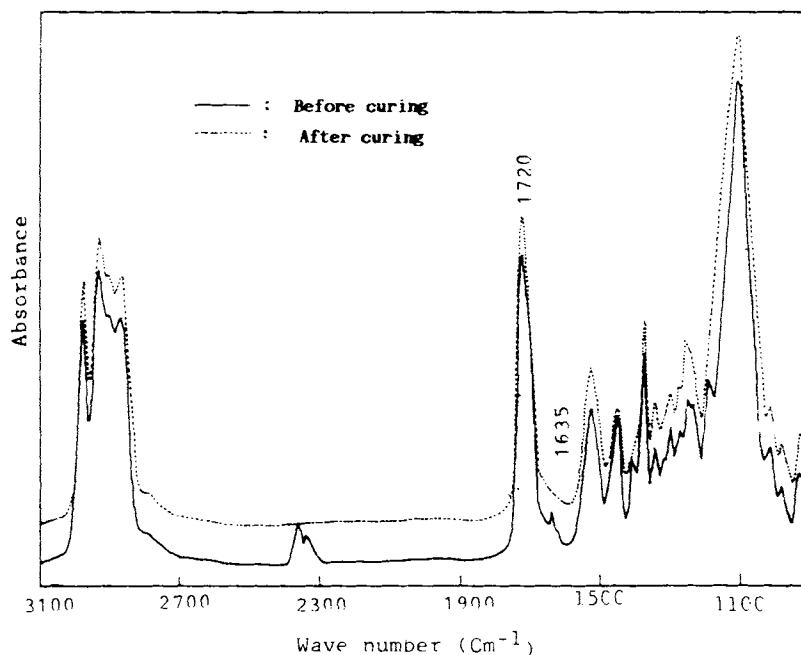
Figure 1   Infrared spectra of prepolymer (HMDI/HEA/PPG) before and after UV curing.

The degree of cure of the urethane acrylate pre-polymers (HMDI/HEA/PPG and/or PBD) after exposure to UV was measured in terms of gel content. The results are shown in Figure 2. Figure 2 illustrates the change in gel content as a function of curing time for three urethane acrylates consisting of different PPG/PBD compositions. It is seen that there are dramatic increases in gel content up to about 80% within 0.5 s, but thereafter there are very small gains in gel contents with further increasing time, and the gel content could reach about 90% regardless of the polyol type used. It is generally accepted that a gel content of 90–96% indicates a complete cure of the coating on the fiber. The rather lower gel contents of the urethane acrylates films in this study may be related to several factors including sample thickness, UV intensity, and photoinitiator content, but the effect of those factors was not investigated.

Refractive Index

The refractive indices of several formulated UV-curable coating films are summarized in Table III. The effect of diluent content on the refractive index is clearly seen from the table. In the urethane acrylates using PPG as diol, the refractive index decreased slightly with increasing diluent (AEHE) content. The formulation of PBD-based urethane

prepolymer shows a higher refractive index than that of PPG-based urethane prepolymer, when the same content (23 wt %) of AEHE was used.

It is seen that the refractive index of the formulation was decreased as the ratio of PBD/PPG is decreased in the mixed diols. It should be pointed out that most of the formulations show refractive indices equal to or larger than 1.46 and thus can be applied in primary fiber coatings, except for the formulation of the HMDI/HEA/PPG system consisting of AEHE more than 17 wt %.

Dynamic Mechanical Behavior

Effect of Prepolymer Structure

It was mentioned that the primary coating for optical fiber should have a low modulus of the order of 10^8 dyne/cm^2 (10 MPa) at low temperature to reduce the microbending losses. The dynamic mechanical behaviors of the urethane acrylate films containing two different polyols in the absence of diluent acrylate monomer are shown in Figures 3 and 4. Figure 3 is the storage modulus (E') change with temperature. The storage moduli of the PPG-based urethane prepolymer showed slightly higher values than did the PBD-based urethane prepolymer. The storage moduli of the urethane prepolymer consisting of both PBD and PPG vary from 4×10^8 to 6×10^9 dyne/cm^2 at $-40°C$. As shown in Figure 3, when
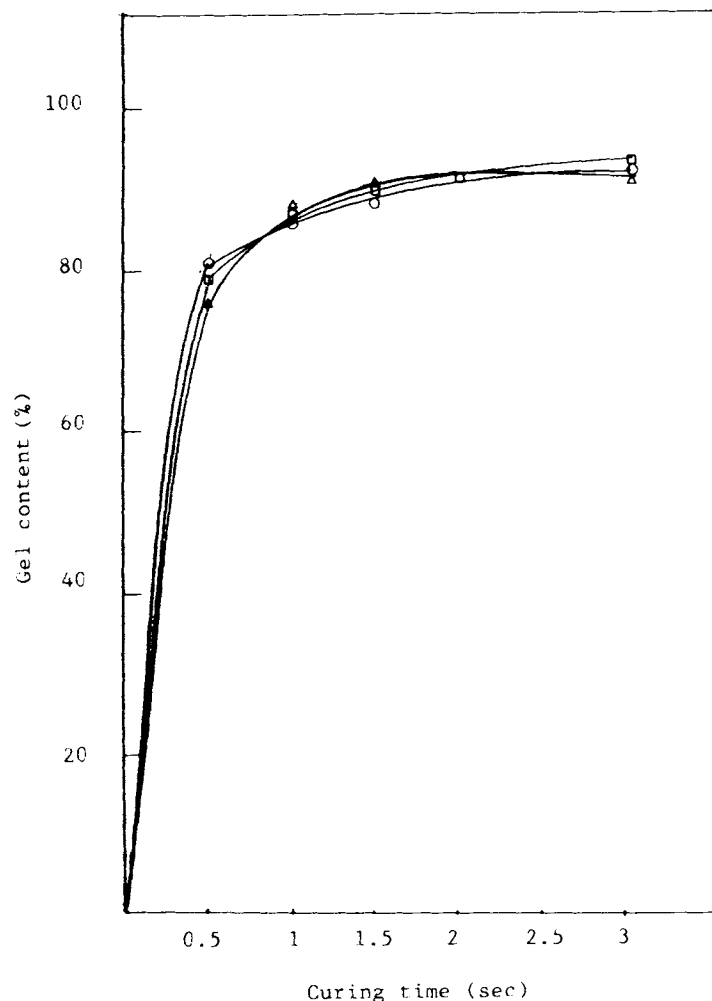
Figure 2 Gel content of dry film as a function of curing time (○) PPG (10%)/PPG (90%); (□) PPG (50%)/PBD (50%); (△) PPG (80%)/PPG (20%).

the content of PBD is above 50 mol % in the mixed polyols, the moduli of the urethane prepolymers are of the order of 10^8 dyne/cm² and of relatively low values.

Figure 4 shows the tan δ change with temperature. The peak position related to T_g shifted toward lower temperature as the ratio of PBD is increased in the mixed polyols. The lower shift of T_g for PBD-richer urethane prepolymer was interpreted as due to the effect of the easier micro-Brownian motion of flexible PBD chains rather than that of PPG chains. The T_g values estimated from the maximum peak of E'' is given as −68, −62, −60, and −48°C for PBD-, PBD50/PPG50-, PPG80/PPG20-, and PPG-based urethane prepolymer, respectively. These results mean that all the urethane prepolymers prepared in the study can be applied for use in the primary optical fiber coating to reduce loss

and increase buffer function, since the urethane prepolymers showed low moduli even at low temperature, say, below −40°C.

The viscosity of the liquid urethane acrylate prepolymer before curing became very high (higher than 1000 cps) as the concentration of PBD was larger than 50 wt % when the mixed diols were used for the prepolymer. In the effect of the prepolymer structure on viscosity, it is concluded that the concentration of PBD below 50 wt % is desirable for prepolymer to assure low viscosity, which leads to good processability for coating (see Table III).

Effect of Different Isocyanates

The effect of different isocyanates on the dynamic mechanical behavior of the urethane prepolymer is shown in Figures 5 and 6. In this case, PPG was
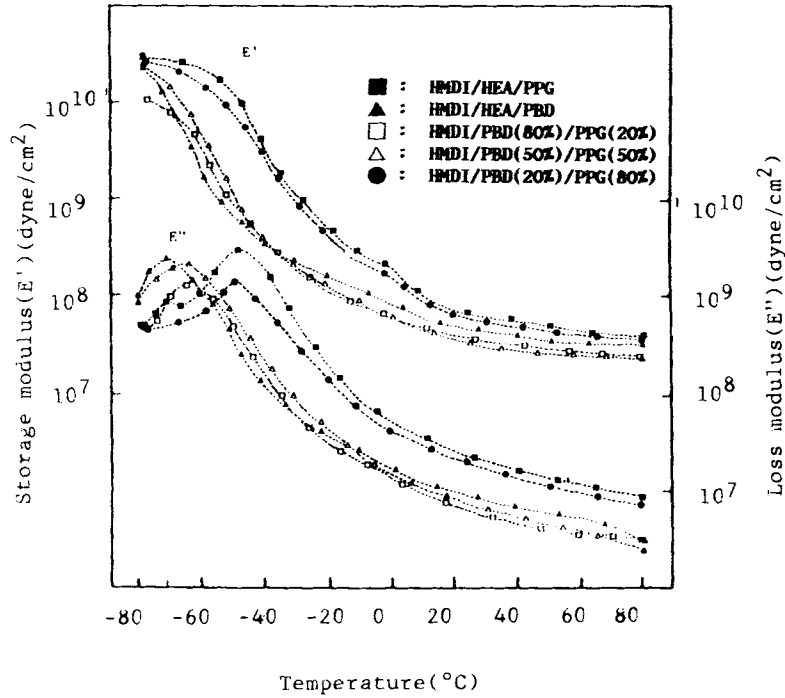
Figure 3   Effect of prepolymer structure on E' and E'' for the primary coating material.

used as polyol. The IPDI/PPG prepolymer shows slightly lower E' over the temperature range of −50 to 80°C than does the HMPD/PPG prepolymer, but the trend is reversed below −50°C. It should be remarked, however, that the effect of different iso-cyanates is not significant when compared to the effect of polyol types on the dynamic mechanical properties, especially in case of E'' of the urethane prepolymer. A similar trend was shown in Figure 6 in the tan δ change as a function of temperature.
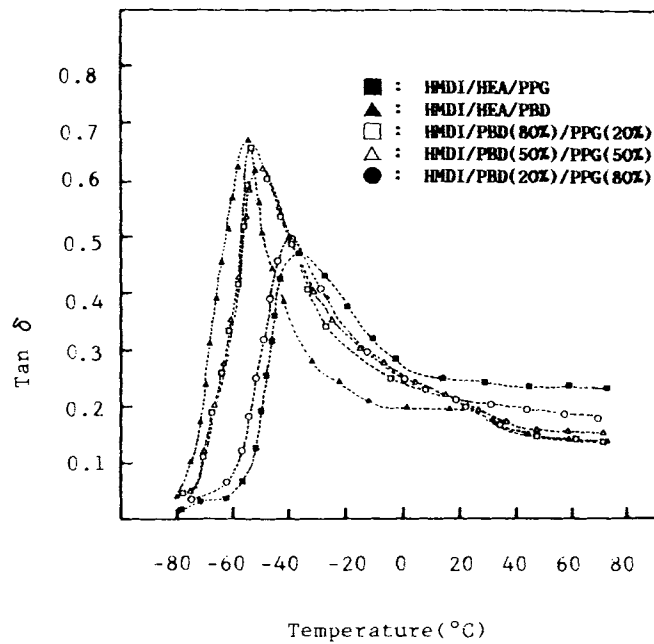
Figure 4   Effect of prepolymer structure on tan δ for the primary coating materials.
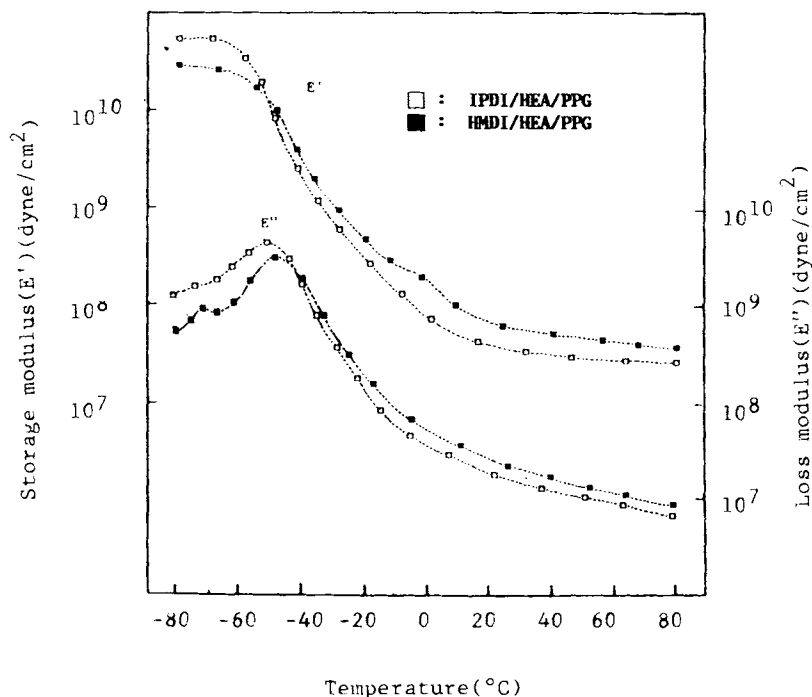
Figure 5 Relationship between moduli (E' and E'') and temperature for the primary coating materials.

Effect of Diluent Structure

Diluents are used in UV-curable systems to provide mainly viscosity control of the formulation. They are also important in determining the speed of cure, cross-link density, and thickness of the cured coating films.

Figures 7 and 8 show the effect of diluent structure on the dynamic mechanical behavior of the urethane acrylate-coating films with various diluents (VP, LMA, AEHE, and ABE; for notations, see Table II). Here, the coating films were formulated from 91 wt % HMDI/PPG/HEA prepolymer and 9 wt % of diluent. These results show that the maximum tan δ or E'' (i.e., T_g) is almost constant at $-48°C$ regardless of the diluent structures, meaning that any of the above monofunctional diluents does not affect on the structure of the flexible polyol, PPG, which is closely related to the micro-Brownian motion of the urethane acrylates. The E' of the urethane acrylates is increased in the order of the formulations using VP > LMA > AEHE. This result may be due to the structural feature of the diluents, since VP contains a rigid aromatic functional group, whereas LMA or AEHE has more flexible aliphatic group.

The urethane acrylate prepolymer without the diluent showed a higher modulus than did the formulated coating with AEHE, even though the dil-

uent-free urethane acrylate showed lower E' than did the urethane acrylate formulated with VP or LMA. Thus, it is concluded that the AEHE is the
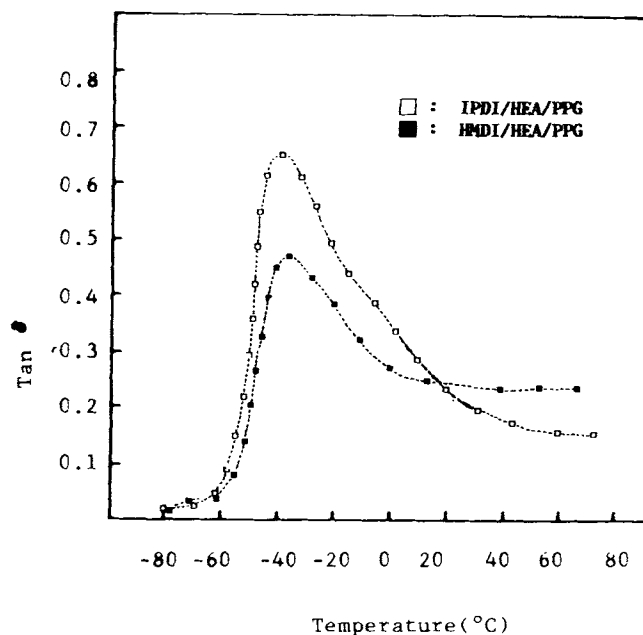

Figure 6 Relationship between tan δ and temperature for the primary coating materials.
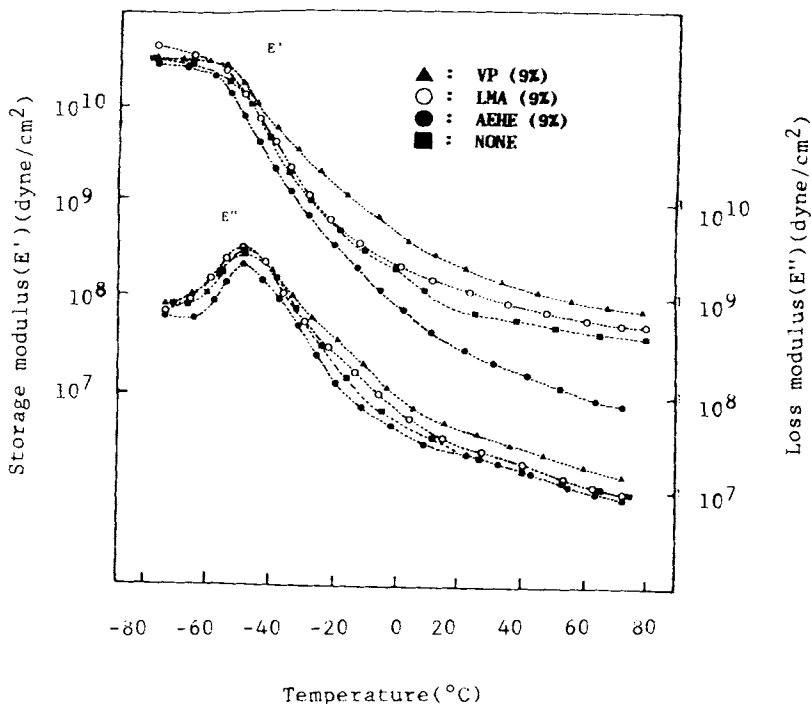
Figure 7   Relationship between modulus and temperature of coating material containing prepolymer (HMDI/HEA/PPG) and different kind of diluent.

most desirable diluent for formulation of the urethane acrylates in this work.

Figure 9 shows the storage modulus of the urethane acrylate prepolymer with ABE and AEHE of 17 wt % composition. The formulation from ABE containing less of the methylene group, compared to AEHE, shows higher E', but the maximum tan δ peak shows no significant difference in between (see
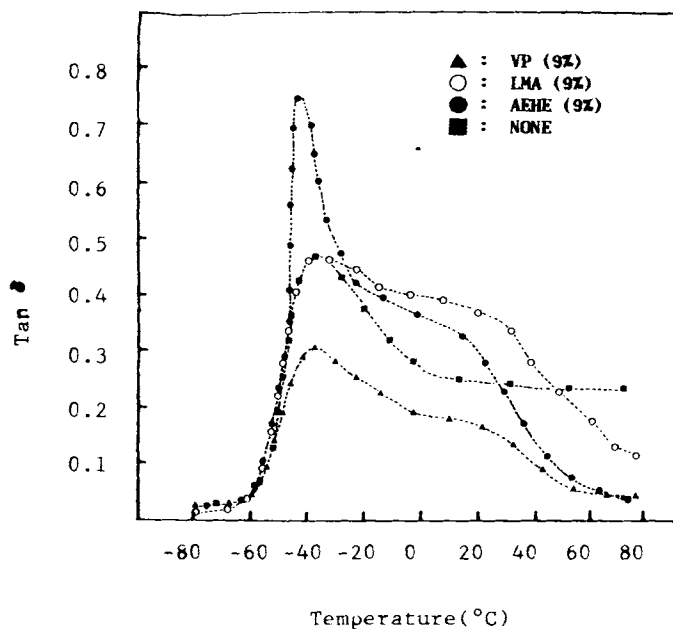

Figure 8   Relationship between tan δ and temperature of primary coating material containing prepolymer (HMDI/HEA/PPG) and different kind of diluent.
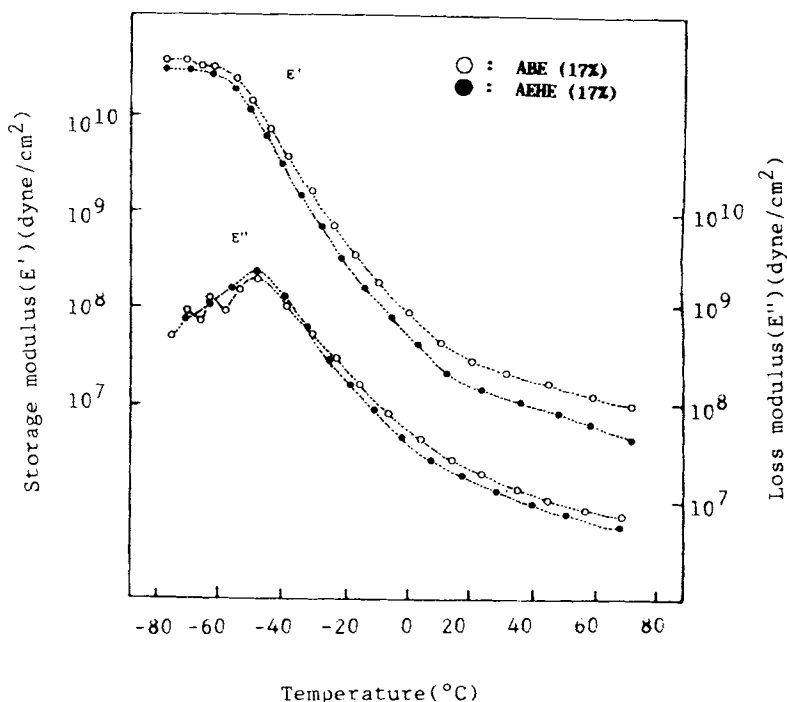
Figure 9   Relationship between modulus and temperature of coating material containing prepolymer (HMDI/HEA/PPG) and different kind of diluent.

also Fig. 10). This again means that the AEHE is the most desirable diluent for formulation for the primary fiber coating because of its long flexible side chains.

Effect of Diluent Contents

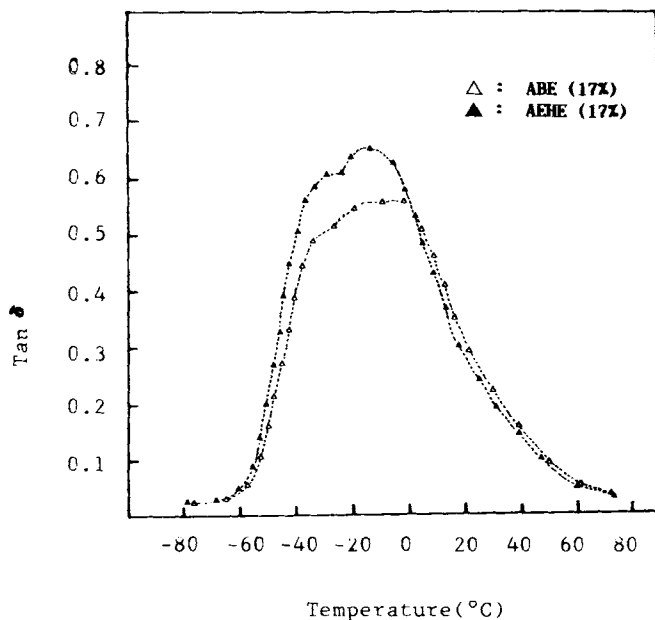Figure 11 shows the effect of the diluent contents on the storage modulus for the HMDI/HEA/PPG

Figure 10   Relationship between tan δ and temperature of coating material containing prepolymer (HMDI/HEA/PPG) and different kind of diluent.
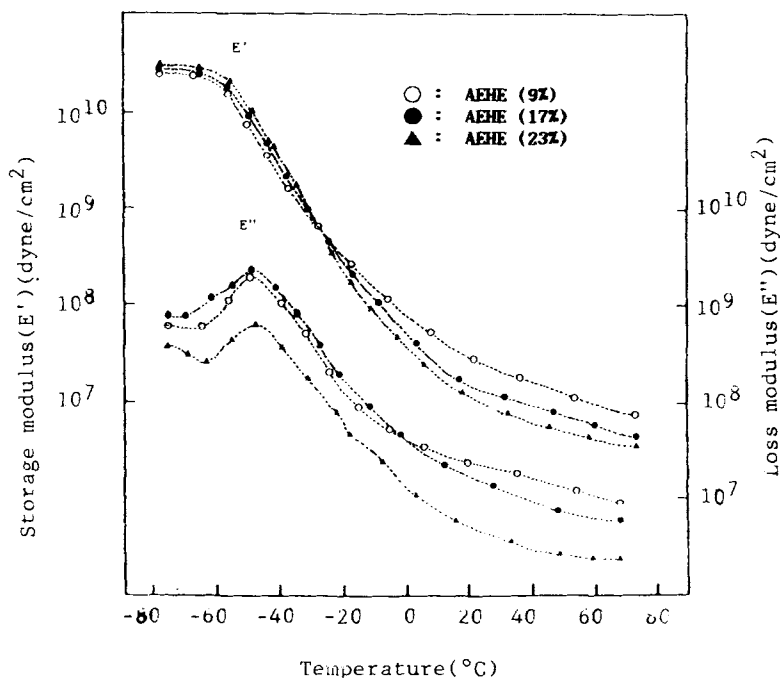
Figure 11 Effect of diluent (AEHE) contents on E'' and E' for primary coating material with prepolymer (HMDI/HEA/PPG).

prepolymers. AEHE was used as a diluent for formulation in the urethane acrylate system. As the diluent contents increases, the modulus, E', increases at low temperature below $-30°C$ but decreases above $-30°C$. The result may be related to the decreased structural order resulting from the difficulty in regular molecular packing because of the long side chains at higher temperature. The latter speculation may be proved by considering the decreasing refractive indices of the formulations with increasing AEHE contents, which is closely related to the decrease in densities of the formulations, as mentioned in Table III. The reason why the E' at lower temperature below $-30°C$ increases with increasing diluent content is not clear at the present moment. More detailed studies should be made.

It is noteworthy that the maximum loss peak (E'') is almost unchanged around $-48°C$ both for the formulations with and without AEHE. Similar results were already observed in Figures 7 and 8. The phenomenon was explained by the fact that the AEHE as diluent does not significantly affect on the micro-Brownian motion of the flexible chain of polyol within the urethane acrylate prepolymer. It may be assumed that the formulation system is composed of complex multiple phases including the soft segment, hard segment, and diluent phases.

Viscosity

It has been stressed that the liquid UV-curable formulations before UV curing show Newtonian fluid behavior and the low viscosity (below 1000 cps) is required for use in optical fiber coating. Figure 12 shows the viscosity change with temperature of the urethane prepolymer (HMDI/HEA/PPG)/diluent (AEHE) formulation of 83/17 wt % composition. The viscosity was very sensitive to temperature. The viscosity of the prepolymer without diluent is given above 1000 cps at 70°C. This result implies that the use of diluent is very essential for fiber coating.

Figure 13 shows the viscosity of the liquid formulation of urethane acrylate prepolymers and the AEHE diluent. In this case, 10 mol % of PBD and 90 mol % of PPG were used as polyols. The viscosity decreased with increasing AEHE content. The rheological behavior showed Newtonian behavior.

CONCLUDING REMARKS

The UV-curable urethane acrylates for buffer coating for optical fiber was formulated from the urethane prepolymer, diluent, and photoinitiator. The properties of the urethane acrylate coating such as
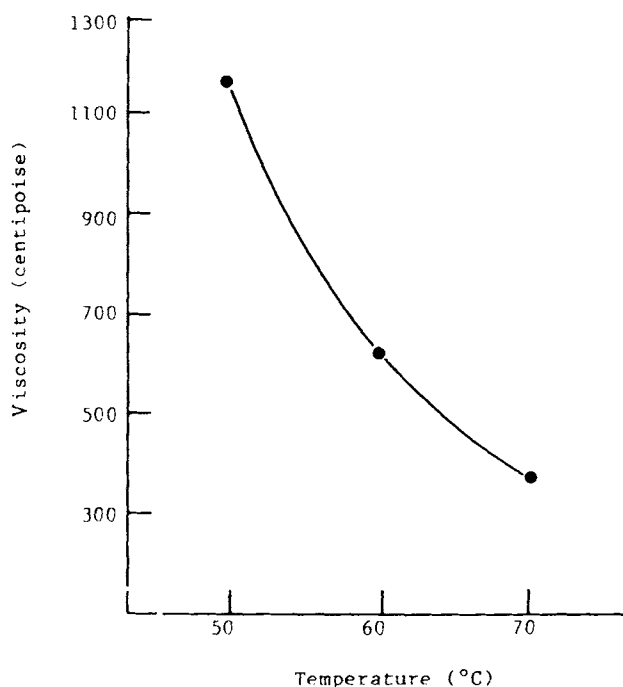
Figure 12 Relationship between viscosity and temperature for the primary coating material (HMDI/HEA/PPG [83%]: AEHE [17%]).

polymer started from polybudiene diol (PBD) or polypropylene oxide diol (PPG), which was formulated with several different diluents and 2,2-dimethoxy-2-phenyl acetophenone as a photoinitiator.

The gel content of the UV-curable urethane acrylates reached to about 90%. It was observed that the refractive index of the formulated coating film decreased with increasing diluent content. Since the refractive index above 1.46 is required for use in the primary coating of the step index optical fiber, it should be suggested that a proper type and content of diluent should be used. The storage modulus of the PPG-based urethane acrylate prepolymer film showed slightly higher values than did the PBD-based urethane prepolymer.

Most of the urethane acrylate prepolymers prepared in the study could be applied in the formulation of primary fiber coating and showed good properties of buffer function, since the formulations had low T_g and low modulus even at low temperature, say, below $-40°C$, high refractive index, and low viscosity.

The effect of different isocyanates [4,4'-dicyclohexylmethane diisocyanate (HMDI) or isophorone diisocyanate (IPDI)] on the dynamic mechanical behavior of the urethane prepolymer film is not significant when compared to the effect of polyol types on their dynamic mechanical properties. The effect of diluent structure and contents on the dynamic mechanical behavior of the coating film containing urethane acrylates (HMDI/HEA/PPG) was neg-
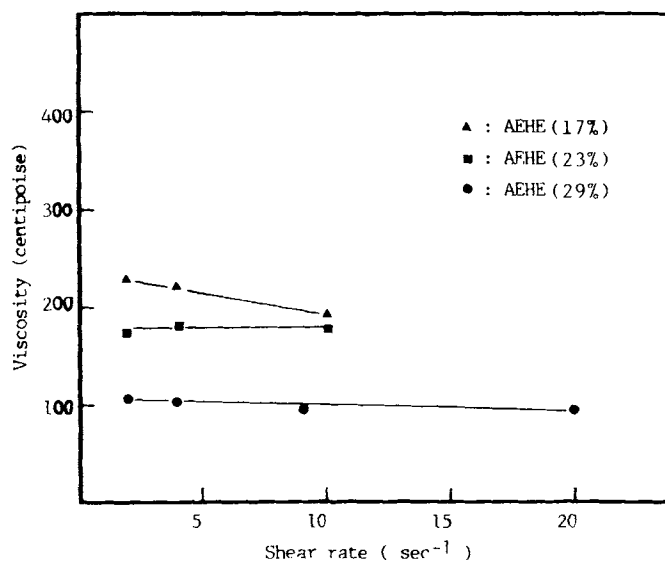
modulus, refractive index, and viscosity were dependent on the type and content of urethane acrylate prepolymer and of diluent and the overall composition of the formulation. We studied urethane pre-

Figure 13 Viscosity vs. shear rate for the primary coating materials formulated with prepolymer [HMDI/HEA/PBD/PPG(10/90)]/AEHE diluent at 70°C.

ligible. It was found that the HMDI and AEHE are the desirable isocynate and diluent, respectively, in the formulation of the primary optical fiber coating material.

It was observed that the maximum loss peak (E'') of the urethane acrylate films is almost unchanged around $-48°C$ regardless of being with or without AEHE. The phenomenon was explained by the fact that the AEHE as diluent does not significantly affect on the micro-Brownian motion of flexible polyol chains in urethane prepolymer. The viscosity of the formulated liquid mixture before UV curing, when AEHE is used as diluent, decreased with increasing AEHE content. It was observed that the rheological behavior of the formulated liquid mixture shows Newtonian behavior. For the effect of mixed PBD/PPG diols in the urethane acrylate, it was observed that the modulus decreases but the viscosity increases as the PBD content increases.

Thus, the desirable composition of PBD, when the mixed polyols are used, should be below 50 wt % for optimum formulation. In conclusion, the urethane acrylate prepolymers and diluents were formulated to meet demanding requirements of viscosity, modulus, T_g, and refractive index dictated by primary coating applications for optical fiber.

REFERENCES

1. W. B. Gardner, *B.S.T.J.*, **54**(2), 457–465 (1975).
2. D. Gloge, *B.S.T.J.*, **54**(2), 245–262 (1975).
3. T. Naruse and Y. Sugawara, *Electron. Lett.*, **13**, 153–154 (1977).
4. T. E. Bishop, U.S. Pat. 4629-87 (1986).
5. K. Nakamura, N. Murata, and T. Maruno, in *Proceedings of the Conference on Radiation Curing ASIA (CRCA '88)*, 1988, pp. 131–135.
6. T. Kimura and S. Yamakawa, *Electron. Lett.*, **20**, 201–202 (1984).
7. T. Kimura and S. Yamakawa, *J. Polym. Sci.*, **24**, 1161 (1986).
8. A. Lilaonitkul and S. L. Cooper, *Advances in Urethane Science and Technology*, K. C. Frish and S. L. Reegen, Eds., Technomic, Westport, CT, 1979 Vol. 7, p. 163.
9. C. Bulestein, *Polym. Plast. Technol. Eng.*, **17**, 83 (1981).