



Synthesis and characterization of ultraviolet light-curable resin for optical fiber coating

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Abstract

UV-curable polydimethylsiloxane epoxy acrylate (PSEA) and polyethylene glycol urethane acrylate (PGUA) were synthesized and characterized by ¹H-NMR and FTIR spectra. PGUA, PSEA and trimethylolpropane triacrylate (TMPTA) were mixed in different proportions to modify the properties of blends to prepare optical fiber coating. Formulation was optimized by the orthogonal table. When the proportion was PGUA:PSEA:TMPTA = 10:4:3, it was used for a single coating (OFC-6). However, the proportion PGUA:PSEA:TMPTA = 8:3:2 was used for a primary buffer coating. The rheological behavior and the selection of photoinitiators for OFC-6 were also discussed. The photopolymerization of OFC-6 was inspected by the FTIR spectrum. Results show OFC-6 film is completely cured after irradiated 5 s. The thermal behaviors of the cured film were also investigated by TGA, DMA, etc.

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1. Introduction

Optical fibers made from drawn glass have been used as a reliable transmission medium in telecommunications cables. Glass optical fibers are widely used because they have the ability to carry large amounts of information over long distances [1].

To facilitate these long-distance transmissions, optical fiber waveguides have been coated with plastic compositions of various materials in order to protect the fiber and increase its tensile strength. Generally, to accomplish this, optical glass fibers are frequently coated with two superposed coatings. The coating which contacts the glass is a relatively soft, primary coating that must satisfactorily adhere to the fiber and be soft enough to

resist microbending especially at low service temperatures. The outer, exposed coating is a much harder secondary coating that provides the desired resistance to handling forces yet must be flexible enough to enable the coated fiber to withstand repeated bending without cracking the coating [2].

Coatings are applied to the fiber in-line during fiber drawing. As the state of fiber drawing technology has allowed for increased drawing speeds to effectuate longer and thinner optical fibers, however, the need for coating compositions that can cure at faster rates coincident with the faster draw speeds has become more urgent. Therefore, it is highly desired for an uncured primary coating to be capable of a high cure speed.

While the conventional coating compositions have been adequate for most applications [3–6], it would be desirable to be able to formulate coating compositions for optical glass fibers that not only possess good adhesion to glass, but also maintain a high rate of cure.

Further, the cure primary coating should exhibit heat resistance, weatherability, low water absorption and

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good adhesion to glass to prevent delamination of the coating from the optical fiber [7]. Delamination can be caused by excessive moisture. This is particularly devastating to optical fiber because the delaminated coating can slide against the optical glass fiber causing microscopic scratches. Ultimately, such delamination can result in a loss of optical fiber transmission.

To reduce such delamination, adhesion promoting additives have been incorporated into coating compositions [8]. Typically silane adhesion promoters have been used. However, it is known in the field that the use of adhesion promoters can reduce the speed of cure of a coating composition.

In the present work, above problems can be solved by UV-curable polydimethylsiloxane epoxy acrylate (PSEA) [9], which containing acrylic ester groups, linked to the siloxane chain as pendant units, give the PSEA reactivity, absorptivity, coupling properties, etc. This compound combines the properties of silicones with the fast crosslinking ability of acrylates. Furthermore, it owns unique properties, such as, low glass transition temperature (T_g), low surface tension and surface energy, low solubility, low dielectric constant, transparent to visible and UV light, very resistant to ozone, and stable against atomic oxygen even oxygen plasmas.

In this study, different proportions of PSEA are blended with polyethylene glycol urethane acrylate (PGUA) and trimethylolpropane triacrylate (TMPTA) to prepare different optical fiber coating with desired properties. The optimum optical fiber coating is studied by $^1\text{H-NMR}$ and Fourier transform infrared spectroscopy (FTIR), thermogravimetric analyzer (TGA) and dynamic mechanical thermal analysis (DMA).

2. Experimental

2.1. Materials

Hydrogen-containing polydimethylsiloxane (H-PDMS, hydrogen amount 1.26% per mole chain unit) was supplied by Wuhan University, China. Allyl glycidyl ether (AGE) was obtained from Acros, USA. TMPTA was supplied by UCB, Belgium. Benzil dimethyl ketal (BDK) was supplied by Ciba Geigy, Switzerland. Acrylic acid (AA) was purchased from Dongfang Chemical Factory, Beijing. Toluene-2,4-diisocyanate (TDI), polyethylene glycol ($M_n = 1000$), beta-hydroxypropyl acrylate (HPA), dibutyltin dilaurate, methoxyphenol and benzophenone (BP) were purchased from the first reagent Co. of Shanghai, China. Optical fiber coating 950-075 and 950-042 were from DSM (Desotech Inc., Elgin, USA). All solvents are reagent grade or are purified by standard methods.

2.2. Synthesis of polydimethylsiloxane type epoxy resin (PSE)

H-PDMS, AGE (1.05 equivalents of Si-H), 0.8 wt% of Pt-catalyst and toluene were placed in a 250 ml flask along with a low stream of nitrogen, then the mixture was heated to 130 °C and stirred until the absorption peak of the Si-H peak (2140 cm^{-1}) in the FTIR spectra disappeared. The solvent and the unreacted AGE were removed by distilling at 120 °C in vacuum. The obtained product was a colorless viscous liquid, PSE [$\eta_{25\text{ °C}} = 1.6$ Pa S, epoxy value (EV) = 0.5]. The molecular structure was confirmed by $^1\text{H-NMR}$ and FTIR spectrum. The determination of the epoxy value was carried out using a potentiometric titration as described in the literature [10]. EVs are calculated using the equation:

$$\text{EV (mol/100 g)} = C(v - v_0)/10W$$

where C is the concentration of $\text{HClO}_4\text{-HAc}$ standard solution (mol/l), v_0 and v are, respectively, the blank and sample consumption of $\text{HClO}_4\text{-HAc}$ standard solution (ml), and W is the weight of sample used (g). The content of active hydrogen is determined by the modified Zerewitinoff method [11].

$^1\text{H-NMR}$ (CDCl_3 , ppm): 0.07 ppm (Si- CH_3); 0.52 ppm (Si- CH_2 -); 1.69 ppm ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$); 2.52, 2.95 ppm (epoxyethane); 3.58 ppm ($-\text{CH}_2$ -epoxyethane); 3.60 ppm ($-\text{OCH}_2-\text{CH}_2-$).

FTIR (cm^{-1}): 2963, 1409, 1261 (Si- CH_3); 1020–1090 (Si-O-Si); 1289, 2975 ($-\text{epoxyethane}$).

2.3. Synthesis of polydimethylsiloxane epoxy acrylate

PSE, acrylic acid (AA) [mole ratio = 1:1.08] were dissolved in toluene and reacted at 110 °C under stirring. After 4 h, the conversion reached 94% by determining the epoxy value or the acid value. The product was cooled to 60 °C, then toluene and unreacted AA were discarded by reduced pressure distillation. The remainder is straw color viscous liquid, PSEA ($\eta_{25\text{ °C}} = 3.0$ Pa S).

$^1\text{H-NMR}$ (CDCl_3 , ppm): 0.08 ppm (Si- CH_3); 0.53 ppm (Si- CH_2 -); 1.67 ppm ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$); 3.53 ppm ($-\text{CH}_2\text{CH}_2-\text{O}-$); 3.64 ppm ($-\text{CH}_2-\text{OH}$); 3.76 ppm ($-\text{OCH}_2-\text{CH}-\text{O}-$); 5.10 ppm ($\text{CH}_2-\text{CH}-\text{O}-$); 5.78 ppm ($\text{H}_2\text{C}=\text{C}$); 6.09, 6.13 ppm ($\text{CH}_2=\text{CH}-$).

FTIR (cm^{-1}): 3420 (HO-); 2963, 1409, 1261 (Si- CH_3); 1719 (carbonyl), 1020–1090 (Si-O-Si); 1625, 1610, 930 ($\text{C}=\text{C}$).

2.4. Synthesis of polyethylene glycol urethane acrylate

Under nitrogen atmosphere, polyethylene glycol (0.2 mol, 200 g), HPA (0.2 mol, 26.0 g) and methoxyphenol (1000 ppm over total amounts of the reactants) were

added dropwise into a flask containing TDI (0.3 mol, 52.5 g) and 0.1 wt% dibutyltin dilaurate at room temperature, then stirred at 70 °C until the disappearance of the isocyanate peak (2270) in the FTIR spectrum, giving a transparent viscous resin.

¹H-NMR (CDCl₃, ppm): 1.78 ppm (Ph-CH₃); 1.91 ppm (CH₂-CH₂-CH₂); 3.57–3.61 ppm (-O-CH₂-CH₂-); 4.08 ppm, 4.25 ppm (-CH₂-CH₂-CH₂-); 5.79, 6.35 ppm (-CH=CH₂); 6.07 ppm (-CH=CH₂); 6.88–7.04 ppm (Ph-H); 7.24, 7.37 ppm (-NH-).

FTIR (cm⁻¹): 3310 (-N-H); 2800–3000, 1454 (C-H, aliphatic); 1720 (C=O); 1603, 1412 (C-C, Ph); 1538 (benzene ring); 1200–1270, 1078 (C-O-C); 876, 811 (C-H, benzene ring); 748 (O=C-O, urethane); 1628, 1615, 932 (C=C).

2.5. Formulation of UV-curable coatings

As indicated in Table 1, various amounts of the three prepolymers were blended to yield 100-part-by-weight batches of each mixture. Then five parts by weight BDK, three parts by weight of a BP/triethylamine mixture (wt%, 1:1), and one part by weight of methoxyphenol were mixed, melted, and added to each batch of prepolymer mixture. These blends were then mechanically mixed to blend the ingredients. The UV-curable coating formulations were stored in opaque containers. Each prepolymer was also formulated in this manner and measurement.

2.6. UV curing of coatings

Glass plates were cleaned and dried, then films approximately 0.1 mm in thickness were cast onto the plates with a “bird type applicator”. The films were irradiated by a high-pressure mercury lamp (1 kW, HPM 15 from Philips, Belgium) built into an UV-CURE device constructed in our laboratory, with a distance of

15 cm from lamp to specimen and at room temperature in N₂ atmosphere.

2.7. Measurements

The viscosity of the products was measured with a QNX Model spinning viscometer (Tianjin Instrument Co., Tianjin, China) with the speed of 750 rpm.

The tack-free time was evaluated as the exposure time required to reach a completely tack-free state by touching the surface with a cotton ball under a weight of 200 g for 30 s after UV exposure.

The degree of unsaturation in the UV-cured film was determined with a MAGNA-IR 750 SPECTROMETER (Nicolet Instrument Co., USA) using the acrylate double bond at 1610–1625 cm⁻¹ by a baseline method. The spectra were normalized with the carbonyl peak at 1719 cm⁻¹ as an internal standard to account for variation in sample thickness and instrument recording. The double bond content of the uncured formulation was defined as 100%.

¹H-NMR spectra were recorded on a 200 MHz instrument (Bruker AC200) using CDCl₃ as solvent and tetramethylsilane as internal standard. GPC data were recorded on a Waters Associated 440 instrument with polystyrene standard for calibration and tetrahydrofuran as the solvent.

After being irradiated, samples were cut into thin slices and put into a basket made of 200 mesh stainless steel net. The gel content of samples were determined by extracting the irradiated samples (*w*₁) in the basket for 48 h with boiling xylene stabilized by 0.2 wt% of antioxidant and with N₂ bubbling to prevent oxidation. The solvent was renewed after the first 24 h of extraction. After the extraction, the basket was washed with acetone. After being dried in a vacuum desiccator at about 70 °C to constant weight, the insoluble residue (*w*₂) was weighed. The average gel content (wt%) in the test was

Table 1
Optimizing the formulation for three prepolymers^a

Number	Component ratio (wt%) ^b			Tensile strength (MPa)	Elongation (%)	Modulus (MPa)	Gel content ^c (%)
	PGUA	PSEA	TMPTA				
1	8 (1)	3 (1)	2 (1)	8.0	132	24.3	31.6
2	9 (2)	3 (1)	3 (2)	10.9	156	27.6	41.4
3	10 (3)	3 (1)	4 (3)	9.6	147	26.2	43.1
4	8 (1)	4 (2)	4 (3)	18.1	139	53.2	41.4
5	9 (2)	4 (2)	2 (1)	6.7	110	24.3	51.3
6	10 (3)	4 (2)	3 (2)	10.9	156	23.1	55.8
7	8 (1)	5 (3)	2 (1)	14.1	100	56.5	52.8
8	9 (2)	5 (3)	4 (3)	17.4	86	80.8	42.7
9	10 (3)	5 (3)	3 (2)	6.4	84	30.9	58.9

^a Every mixture coating is prepared according to the method mentioned. Cast films are irradiated for 30 s.

^b The weight ratios of components are outside the parentheses. The test levels are the numbers inside parentheses.

^c Films are irradiated by UV-lamp for 2 s.

calculated as $100 (w_2/w_1)$. Usually, two or three samples were analyzed to determine the average gel content for a given set of irradiation conditions.

UV absorption spectra were recorded by UV-240 spectrometer (Shimadzu, Japan).

Thermal stability was determined with a TGA (Perkin–Elmer TGA7) over a temperature range of 30–500 °C at a heating rate of 10 °C min⁻¹. DMA was carried out on DMA-7 (Perkin–Elmer DMA7), the size of sample was 50 × 10 × 3 mm³. The measurement was performed at a fixed frequency of 1 Hz over a temperature from -150 to 120 °C with a temperature rate 10 °C min⁻¹.

The tensile properties were measured with an Universal Testing Machine (DCSS000, SHIMADZU) at 25 ± 2 °C. The crosshead speed was 50 mm/min. The dumb-bell shaped specimens were prepared according to ASTM D412-87.

3. Results and discussion

3.1. Optimizing formulation of coatings

Table 1 is a series of prepolymer mixtures that are designed and formulated according to orthogonal table to optimize the formulation for optical fiber coating. Its analysis data are list in Table 2. The data show (1) increasing the content of PGUA increases the elongation and cure rate, but decreases the tensile strength and modulus of film; (2) increasing the content of PSEA increases the tensile strength, modulus and cure rate but decreases the elongation of film. PGUA and PSEA possess the contrary effect on the properties of cured film

Table 2
Data analysis for Table 1

Properties	Levels	PGUA	PSEA	TMPTA
Tensile strength (MPa)	1	40.3	28.5	21.1
	2	32.3	35.7	35.9
	3	26.9	35.3	26.8
	4	-15.4	6.8	21.4
Elongation (%)	1	371	435	326
	2	350	405	412
	3	387	268	370
	4	37	-167	86
Modulus (MPa)	1	133.0	78.1	79.5
	2	132.7	99.6	107.2
	3	80.2	168.2	159.2
	4	-52.8	90.1	79.7
Gel content (%)	1	125.8	115.8	141.6
	2	135.4	148.5	150.0
	3	157.6	154.2	127.2
	4	31.8	38.4	-29.2

except for the high cure speed, which provide an opportunity to blend them together to obtain different coating with desired properties; (3) TMPTA can improve the tensile strength, elongation and modulus except for the cured speed.

After above comparison, resin mixture no. 6 optical fiber coating (OFC-6) was selected as a candidate for a single coating for optical fiber and was studied in later section. Such coating make optical fiber manufacture easier and less expensive than processes involving a primary and a secondary coating. Moreover, mixture no. 1 also could be selected as the candidate for a primary buffer coating.

3.2. Photoinitiators of coating

The choice of photoinitiators is generally governed by (1) absorb the irradiation wavelengths and exhibit the highest extinction coefficients in order to use low amounts of product; (2) the requirement for a high curing speed; (3) in the case where a long-term stability of the material is needed; moreover, one has also to consider the influence of the photolysis products of the initiators upon the photochemical time evolution of the polymerized resin.

Following with above principals, we choose BDK/BP mixture photoinitiators to initiate the polymerization of coating. The combination of photoinitiators exhibit a synergic effect, the quantum yield of polymerization is higher than the sum of the yields corresponding to the two modes of initiation [12]. BDK generates the benzoyl and methyl free radicals through photocission process, these free radicals are more efficient initiators in OFC-6 than BP because they are reactive enough to initiate polymerization of vinyl groups. Moreover, BDK has a broad absorption peak at 315–390 nm, which is in the same range as the UV spectrum of the HPM-15 lamp, as shown in Fig. 1. However, BDK involving make the stability of coating storage deterioration or gelation through “dark reaction”. This problem can be solved by mixing appropriate content BP/triethylamine, hydroxy-anisol and additives into coating. Fig. 1 is the UV spectra of the photoinitiators in chloroform (10⁻³ M), and CFO-6 without photoinitiators and emission spectrum from Philips HPM-15 lamp. It shows OFC-6 has absorption band at 210 nm, which cannot shield BDK or BP to form free radical, and the photoinitiators absorb completely the UV light at 350–370 nm of HPM-15 for their appropriate chemical structure.

3.3. Rheological behavior of coating

The viscosity of oligomers is an important parameter in UV-curing technology that affects the cure process and properties of the cured films. When the viscosity of coating is too low, the quartz glass made optical fiber

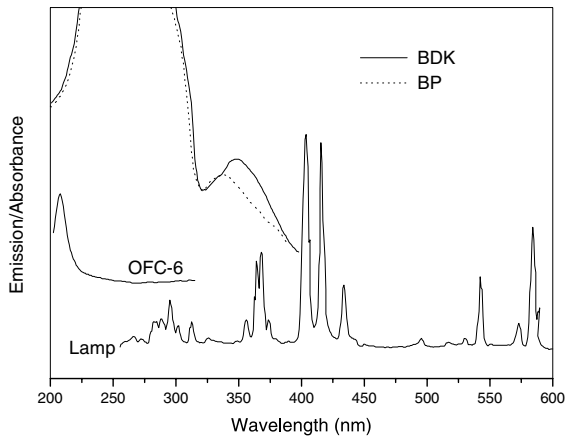


Fig. 1. UV spectra of the photoinitiators in chloroform (10^{-3} M), and CFO-6 without photoinitiators and emission spectrum from Philips HPM-15 lamp.

base is poorly wettable with the difficulty in obtaining an adequate thickness layer. On the other hand, when the viscosity is too high, disadvantages are caused in the removal of air bubbled from the coating layer as well as in respect of the difficulties in obtaining an adequate thickness of the coating layer and decreased workability. The viscosity of a polymer is related to the dynamic extension of the molecules and the segment density within the volume of a molecule and intermolecular chain entanglement. Fig. 2 is the effect of temperature on the viscosity of optical fiber coating OFC-6, 950-075 and 950-042. It shows OFC-6 has low viscosity because the PSEA resin maintains the properties of polydimethylsiloxane, comparing with 950-705 and 950-042 coating. The viscosity of OFC-6 changes sharply from 10,000 cps at 15 °C to 2000 cps at 32 °C, the difference is five times. The viscosity changes of 950-075 and 950-042

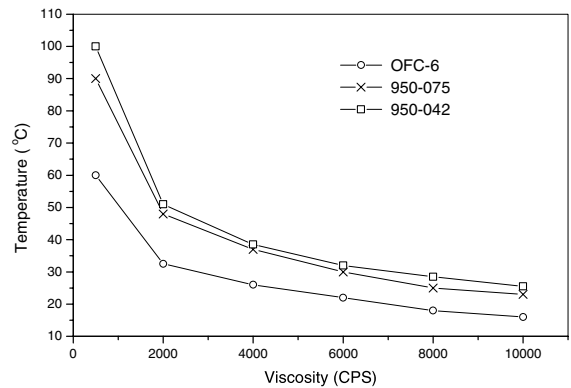


Fig. 2. The effect of temperature on the viscosity of optical fiber coatings.

are similar with small difference in degree as shown in Fig. 2, which go down from 10,000 cps at 28 °C to almost 2000 cps at 50 °C. The changes are also obvious but the scope of temperature is higher than that of OFC-6, which may induce some difficulties at low temperature operation.

3.4. Photocuring process was inspected by the FTIR spectrum

Fig. 3 is FTIR spectra of OFC-6 optical fiber coating before irradiation and irradiated for 5 s. We see clearly that SiCH_3 ($800, 1260 \text{ cm}^{-1}$), SiO (1090 cm^{-1}) are characteristic peaks of silicone. The peaks of NH (3310 cm^{-1}), CH_2 (2930 cm^{-1}), Ph (1600 cm^{-1}), and C=O (1720 cm^{-1}) are characteristic peaks of PGUA. Most important are the peaks at 1632 and 1614 cm^{-1} , which are characteristic peaks of unsaturated double bond. This shows that the content of acryloyl oxygen groups

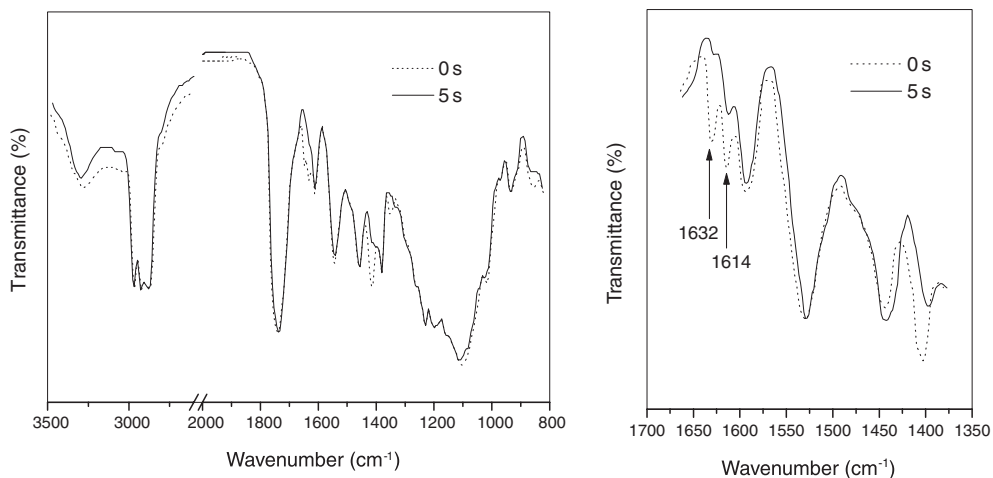


Fig. 3. FTIR spectra of OFC-6 optical fiber coating before UV irradiation and irradiated for 5 s.

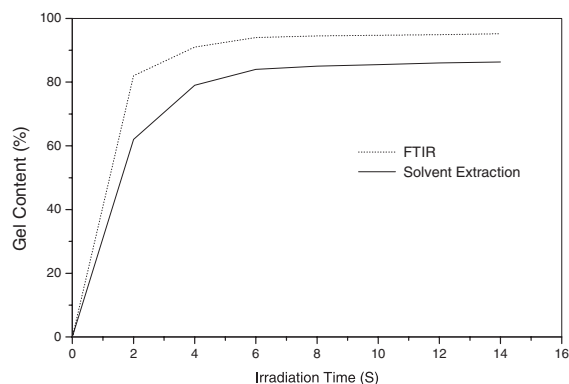


Fig. 4. The gel content of OFC-6 cured films with different irradiation times.

($\text{CH}_2=\text{CHCOO}-$) are large amounts. After UV irradiation for 5 s, it can be found that those peaks disappear completely. It due to curing is almost absoluteness. The double bond is nonexistent. If we calculated the conversion of carbon double bond by absorption, the percent is 92%. This result is higher than the value which is gained by solvent extraction method as show in Fig. 4. This proved the results obtained from FTIR are believable and time saving.

Fig. 4 is the gel content of OFC-6 cured films with different irradiation times. It shows the gel contents obtained from FTIR are higher than that from solvent extraction. OFC coating film touch free after irradiation for 2 s. Extending irradiation time more than 5 s, the gel content change is less. The results are confirmed by the application of OFC coating in spreader (HEATH WAY, UK), the coating speed are 120 m in 1 min.

3.5. Thermal behaviors analyzed by TGA and DMA

OFC-6's thermolysis is shown in Fig. 5. The curve shows OFC-6 has the similar thermal stability to silicone rubber, decomposition temperature is about 280 °C. This is the result of the somewhat unusual molecular structure of the polymer chains, the (Si–O) bond is one of the most thermally stable bonds formed by silicon and has a bond dissociation energy of 462 kJ/mol compared with 359 kJ/mol for (C–O), 347 kJ/mol for (C–C) and 319 kJ/mol for (Si–C) bond. The thermal stability of OFC-6 is thus partly a consequence of the high bond strength of PSEA. When the proportion of coating varying, such as increasing the content of PGUA and TMPTA, the thermal properties described above usually decreases in some degree.

Most polymeric materials can be considered to be viscoelastic solids that exhibit both viscous and elastic properties. DMA is an efficient tool to measure the viscoelastic properties and obtain information about the microstructure of crosslinked networks. The storage

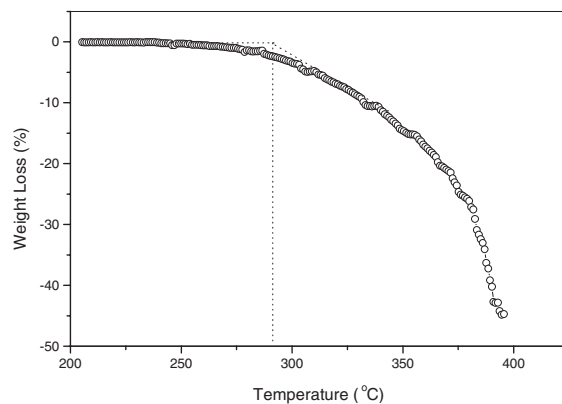


Fig. 5. TGA thermogram of OFC-6 cured film at a heating rate of 10 K min^{-1} .

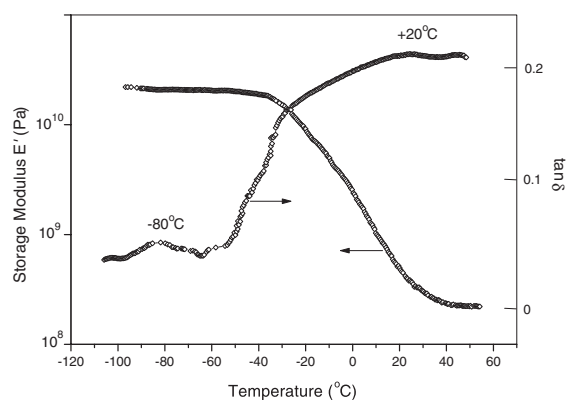


Fig. 6. Dynamic viscoelastic behavior as a function of temperature for OFC-6 cured film.

modulus (E') and the loss factor ($\tan \delta$) for OFC-6 cured film as a function of temperature are shown in Fig. 6. The change of loss factor shows that there are two distinct glass transition temperatures: $T_{g1} = -80$ °C, $T_{g2} = +20$ °C, which declare PSEA has two-phase segregate microstructures. The lower one probably is the characteristics of the siloxane component, and the higher one may be attributed to the crosslinking site which resulted mainly from acrylates.

4. Conclusion

In this study, photosensitive resins are successfully synthesized for the formulation of optical fiber coating. The conclusions are summarized as follows:

1. When the proportion was PGUA:PSEA:TMPTA = 10:4:3, it was used for a single coating. The proportion PGUA:PSEA:TMPTA = 8:3:2 was used for a primary buffer coating.

2. BDK and BP are reactive photoinitiators for OFC-6, this coating has low viscosity and high curing speed. FTIR and gel content measurement show OFC-6 film is completely cured after irradiated 5 s.
3. The excellent high and low temperature behaviors of the cured film ($T_{g1} = -80\text{ }^{\circ}\text{C}$; the decomposition temperature is $280\text{ }^{\circ}\text{C}$) are the advantages of OFC-6.

References

- [1] Bringuler AG, Dameron JB, Navé SD. Eur Patent 1184699, 2002.
- [2] Ryczkowski J, Rayss J. *Vib Spectrosc* 2000;22:95.
- [3] David AC, Dawn H, Walter LR. US Patent 5418016, 1995.
- [4] Jean YB, Sophie GL. US Patent 5650231, 1997.
- [5] Alvin CL. US Patent 6042943, 2000.
- [6] Shustack PJ, Wilson DA. US Patent 6048911, 2000.
- [7] Yoshinori H, Shohei K, Seiji K, Noriyuki M. US Patent 4733942, 1988.
- [8] Timothy EB. US Patent 4849462, 1989.
- [9] Wang WZ. *Eur Polym J* 2003;39:1117.
- [10] Sheng SY, Meng ZC. *React Funct Polym* 2000;45:79.
- [11] McHard JA. In: Kline DM, editor. *Analytical chemistry of polymers*. New York: Interscience; 1959.
- [12] Fouassier JP. *J Chem Phys* 1983;80:339.