

Preparation and Properties of UV-Curable Poly(dimethylsiloxane) Urethane Acrylate.

II. Property-Structure / Molecular Weight Relationships*

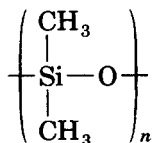
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Synopsis

A series of UV-curable polyurethane acrylate resins based on hydroxy-terminated polydimethylsiloxane (PDMS) soft segments with different molecular weights and various diisocyanate hard segments were synthesized. The products were obtained by employing direct-addition polymerization techniques in a nonsolvent system. The structures of the final products were elucidated by IR and $^1\text{H-NMR}$. The fundamental and physical properties of this type of UV-curable material, the effects on properties by varying the molecular weight of PDMS or the type of diisocyanates, and the effect of using various reactive diluents were widely studied. This resin possessed good optical, electrical insulating, and adhesive properties. The mechanical strength of UV-cured films corresponds approximately to the ratio of hard segments within these materials and the dielectric insulating properties correspond to the chain length of PDMS.

INTRODUCTION

Siloxane polymers and silicone elastomers have received widespread attention since they were introduced commercially. The unique properties of siloxane polymers have led to their application in many diversified fields. Over 15,000 publications throughout the world have appeared on elastomeric siloxane materials.^{1,2} The most common and widely used siloxane polymers are principally based on poly(dimethylsiloxane) (PDMS) whose chemical formula can be given as:



The interesting and useful properties of siloxane polymers are a result of somewhat unusual molecular structure of the polymer chains that consist of alternating silicone and oxygen atoms.³⁻⁵ These backbone chains have an "organic-inorganic" nature, as distinct from typical organic polymers. The repeating unit is characterized by very low molecular forces, ease of rotation, and the relatively long Si—O bond length. These characteristics endow the

*See Reference 21 for Part I.

polymer molecules with unusually high flexibility and the ability to display properties that are fairly constant over a wide service temperature range, say 30–350°C. Moreover, as a result of low intermolecular forces and flexibility, siloxane polymers possess a very low glass-transition temperature ($T_g = -123^\circ\text{C}$).

Soft segments in PDMS-containing copolymers are always in a viscous or a rubbery state at normal service temperatures, while the hard segments are in a glassy or semicrystalline state; there is always complete phase separation between the two.⁶ Polydimethylsiloxane polyurethane resins are likely to be highly separated because of the large differences in the soft and hard segment solubility parameters as well as the lack of hydrogen bonding between hard and soft segments. Thus, the incorporation of low-molecular-weight polydimethylsiloxane as a soft segment material to produce a polyurethane block copolymer gave materials interesting bulk and surface properties because of the properties of the siloxane soft segments. These properties include excellent thermal and oxidative stability, increased impact strength, good release properties, and incompatibility with most organic compounds. Because of their excellent electrical properties at elevated temperatures, silicone elastomers have also been used for insulation on wires and cables. In addition, siloxane-containing materials are noted for their high permeability to gases, high surface activity, and low surface energy. The siloxane segments within copolymers thus tend to migrate to the air-polymer interface⁷ so as to form a hydrophobic surface.

Finally, and perhaps most importantly, PDMSs have very good biocompatibility and, therefore, can serve as biomaterials. They can be used in the presence of blood because they are physiologically inactive,⁸ have very low toxicity, and present no known health hazards. They have been used with success in external prosthesis for encapsulation and some usage as blood-compatible surface coatings.^{4,9} The PDMS-contained copolymers, as a result, can find a wide range of potential applications as elastomers, biomaterials, coatings, and environmentally stable compounds.

In the linear form, PDMS behaves as a viscous liquid above T_g unless it is of an extremely high molecular weight and/or is crosslinked whereby some degree of solid-like character exists.¹⁰ The silicone elastomer network is weak and has poor mechanical properties because of flaws or microcracks produced by the high mobility of chains at room temperature.

A very important way to improve the mechanical strength while still retaining the desired properties of siloxanes is via the controlled synthesis of block or segmented copolymer architecture, thereby introducing some hard segments. This approach has been used extensively by many workers, and various segmented or block siloxane copolymers have been synthesized and characterized. In such systems, the hard segments consist of either crystalline structures with high melting points or amorphous structures with high glass-transition temperatures and include polystyrene,^{11,12} poly(methyl methacrylate),^{11,13} poly(α -methylstyrene),¹⁴ polydiphenylsiloxane,¹⁵ polyamide,¹⁶ polycarbonate,¹⁷ polysulfone,¹⁸ polyurethane,^{19,20} etc. These copolymers behave as thermoplastic materials and their ultimate properties depend on the type and nature of the hard segments, relative molecular weight, composition and/or ratio of the hard and soft segments.

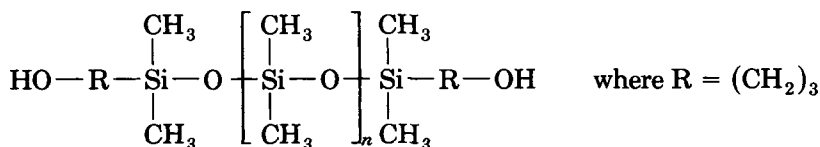
This study aims to improve the mechanical properties by introducing the structure of urethane as a hard segment while still retaining the desired properties of siloxanes so as to obtain a new and excellent UV-curable material.

MATERIALS

Polydimethylsiloxane- α,ω -diol (PDMS) with molecular weights 1000 and 1800 were purchased from Shin-Etsu Chemical Co., Ltd., Japan, and their chemical characteristics are:

Commercial name	X-22-160A	X-22-160AS
Viscosity (cps) 25°C	41.8	33.1
Refractive index 25°C	1.4140	1.4220
Specific gravity 25°C	0.987	0.982
OH value	62	112
\bar{M}_n	1800	1000

Benzoin ethyl ether (BEE), 2,4-tolylene diisocyanate (2,4-TDI), 2-hydroxyethyl methacrylate (HEMA), and trimethylol propane trimethacrylate (TMPTA) were purchased from Tokyo Kasei Co., Japan. 4,4'-Methylene diphenyl diisocyanate (MDI) and 1,6-hexane diisocyanate (HDI) were supplied from MERK-Schuchardt. Butylene-glycol diacrylate (SR238) and isodecyl acrylate (SR395) were purchased from ARCO Chemical Co. All the reagents were used without further purification. The chemical structure of PDMS is



SYNTHESIS

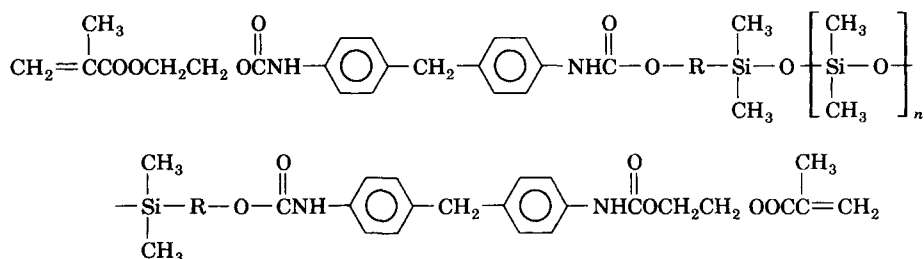
TDI System

The PDMS-based urethane acrylate was synthesized by adding an equimolar amount of PDMS with 0.15 wt% stannous octoate dropwise to 2,4-TDI (i.e., NCO:OH = 2:1) under a nitrogen atmosphere. The reaction flask was equipped with a dropping funnel, a magnetic stirrer, and a condenser with CaCl_2 used as a desiccant. The reaction was maintained at room temperature with a water bath. Two hours later when the absorption peak of OH group in infrared (IR) spectra had disappeared, the temperature was raised to 60°C using an oil bath. An equimolar amount of HEMA with 1.0 wt% hydroquinone as a thermal polymerization inhibitor was added dropwise to the PDMS/TDI adduct. The temperature was kept below 60°C to avoid thermal polymerization and 5 h were needed to complete the reaction. At this time the absorption peak of the NCO group at 2250 cm^{-1} had disappeared completely. More details on the synthesis reaction have been reported in the preceding papers.^{21,22}

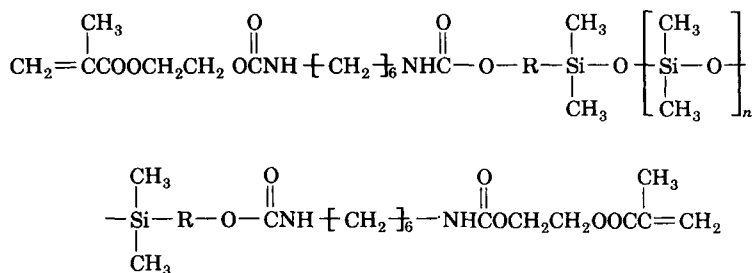
MDI and HDI Systems

The synthesis procedures in MDI and HDI systems are the same as the one in the TDI system, except that the temperature of the second stage was raised to 80°C. The chemical structures of the products are

MDI:



HDI:



Because of the similar reactivity of both NCO groups in MDI and HDI systems, the chemical structures of final products may also be given as:



or



SAMPLE PREPARATION

A certain amount of resin cast on KBr pellets was taken during and after the reaction to facilitate the functional groups analysis and kinetic studies. The viscosity of the final product was measured with 40 wt% acetone after purification, and a 0.5 wt% tetrahydrofuran (THF) solution was prepared for the gel permeation chromatography (GPC) measurement. The mixtures of urethane acrylate oligomer, 1.0 wt% photoinitiator (BEE) and 25 wt% reactive diluent were heated slightly above ambient temperature to ensure homogeneous mixing. The liquid mixtures were poured into two pieces of Mylar films to form membranes of different thicknesses, for example, 0.3–0.4 mm (dry film after UV irradiation) for the tensile test, 0.6–0.7 mm for the electrical test, and about 20–30 μm for the coating tests. All the matrices were treated by water/acid washing before coating.

CHARACTERIZATION METHODS

Infrared Spectroscopy Measurement

The characteristic absorption peaks of functional groups were detected during the synthetic reaction and after UV curing by using a JASCO Model A202 infrared spectrometer under a moisture-free atmosphere. The characteristic absorption peak within the infrared range of 400–4000 cm^{-1} such that C=C stretching at 1635 cm^{-1} was used to determine the reaction extent of the photoinitiated vinyl group, and the NCO group at 2250 cm^{-1} was used to monitor the extent of reaction and in kinetic studies.

$^1\text{H-NMR}$ Spectroscopy Measurement

The NMR spectra were recorded on a JEOL-JNM-PMX60 $^1\text{H-NMR}$ spectrometer instrument. The chemical shift (δ) was given in ppm with tetramethylsilane (TMS) as the internal standard and CCl_4 as a solvent.

Ultraviolet Irradiation

The ultraviolet-curable PDMS-urethane acrylate resin was sandwiched between two Mylar films to maintain the oxygen-free state. The resin with Mylar films was irradiated from one side using a bank of 500W high-pressure mercury lamps (Model USH-500D with 350-nm wavelength manufactured by Ushio Electric Co., Japan) as the irradiation source. An irradiation time of about 10–60 s was found to cure specimens satisfactorily at a distance of 30 cm. The Mylar films were removed after postcuring at least 12 h. The remaining dry films were used for the other tests.

Gel Permeation Chromatography (GPC)

The molecular weight distributions (MWD) of the PDMS urethane acrylate resins were measured using Shimadzu Model LC-5A gel permeation chromatography equipped with an ultraviolet detector (Model SPD-2A, wavelength 254 nm, range 128) and a refractive index detector (Toyo Soda, type RI-1800, range 256). The GPC measurements were performed using tetrahydrofuran as mobile phase with three Styragel columns: G1000HLX, G2000HLX, and G2500HLX at a flow rate of 1 mL/min at 25°C. Because the Mark-Houwink-Sakurada constants are uncertain, the number-average and weight-average molecular weights were calculated on the basis of the molecular weight-retention volume curve of monodisperse polystyrene standards. The area of the GPC curve was approximately proportional to the amount of resin contained in the solvent.

Viscosity

The viscosity of resin with 40 wt% acetone was characterized using a Brookfield viscometer (Model LVF) at 25°C. As expected, the addition of reactive diluents resulted in a large decrease in bulk viscosity.

Uniaxial Stress-Strain Measurement

Room temperature uniaxial stress-strain data, including tensile strength, Young's modulus, and elongation at break, were obtained using an Instron Universal Testing Machine (Model 1130). The measurements following ASTM-D2370-82,²³ were carried out with a crosshead speed of 5 cm/min, chartspeed 100 cm/min, and an original distance 2 cm between the two crossheads. All the reported data were the average of five tests with a samples size of $1.5 \times 10 \text{ cm}^2$.

Dielectric Properties

The volume resistivities of UV-curable films were obtained at 23°C by using a volume resistivity tester of type TR8601 from Takeda Riken Co. The test voltage was 500 V and the charge time 1 min. Dielectric constant, dielectric dissipation factor ($\tan \delta$), and dielectric loss were tested according to ASTM-D150 with frequency 1 KHz and ratio 1×10^{-9} at 23°C.

Thermal Properties

The decomposition temperatures of UV-curable films were obtained by DuPont 1090B thermal analyzer with 951 Thermogravimetric analyzer at a heating rate 20°C/min and test range 50–700°C under a nitrogen purge. The sample weights were about $18 \pm 2 \text{ mg}$.

Solvent Extraction

The gel fraction of the UV-cured samples, about 2–3 g, was determined by Soxhlet extraction using tetrahydrofuran for 24 h at 80°C. The insoluble part was dried for about 2 d and the gel fraction was weighed.

$$\text{Gel fraction} = W/W_o \times 100\%$$

where W : weight of resin after extraction and W_o : weight of original resin.

RESULTS AND DISCUSSION

IR Spectra Analysis

The addition-reaction of polydimethylsiloxane- α,ω -diols and 2,4-TDI/HEMA have been previously reported.²¹ The NCO group in the para position was far more reactive than that in the ortho position in TDI system. Although there was no TDI-like steric effect in MDI and HDI systems, the NH group which could hydrogen bond to either ether linkages or ester carbonyl groups might also induce a partially crystalline structure.²⁴ Therefore, the reaction temperature should be maintained at 80°C.²⁴ The IR spectra of final products are shown in Figures 1 and 2.

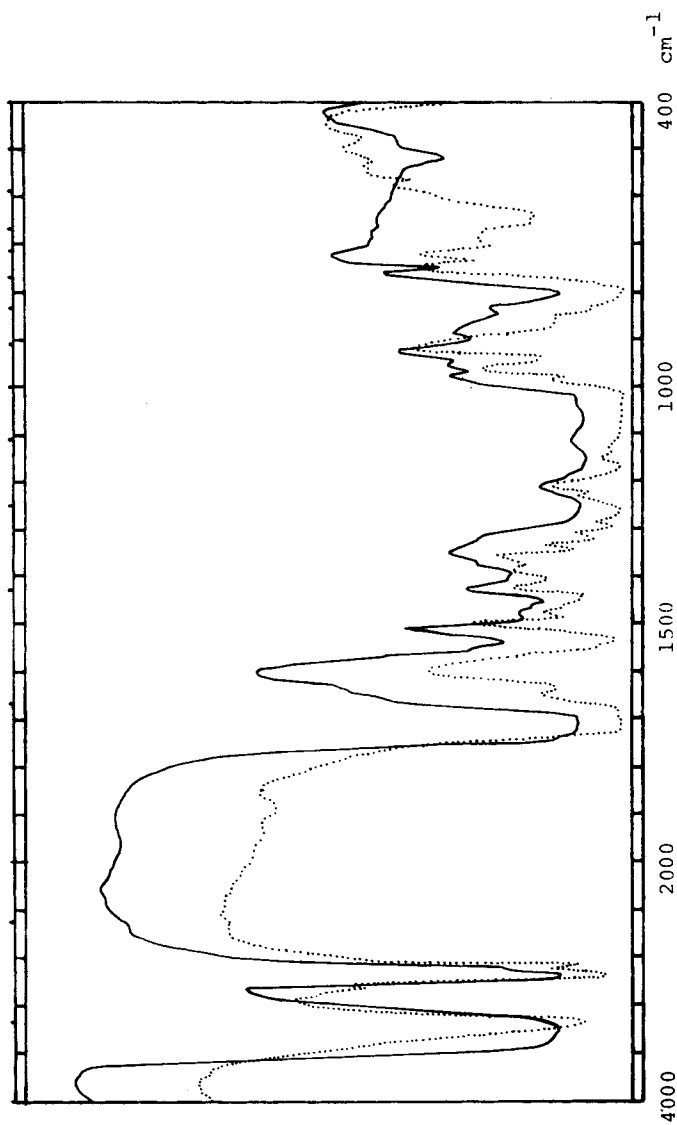


Fig. 1. Infrared spectra of pure resin with (—) and without (···) photocuring (PDMS1800/MDI).

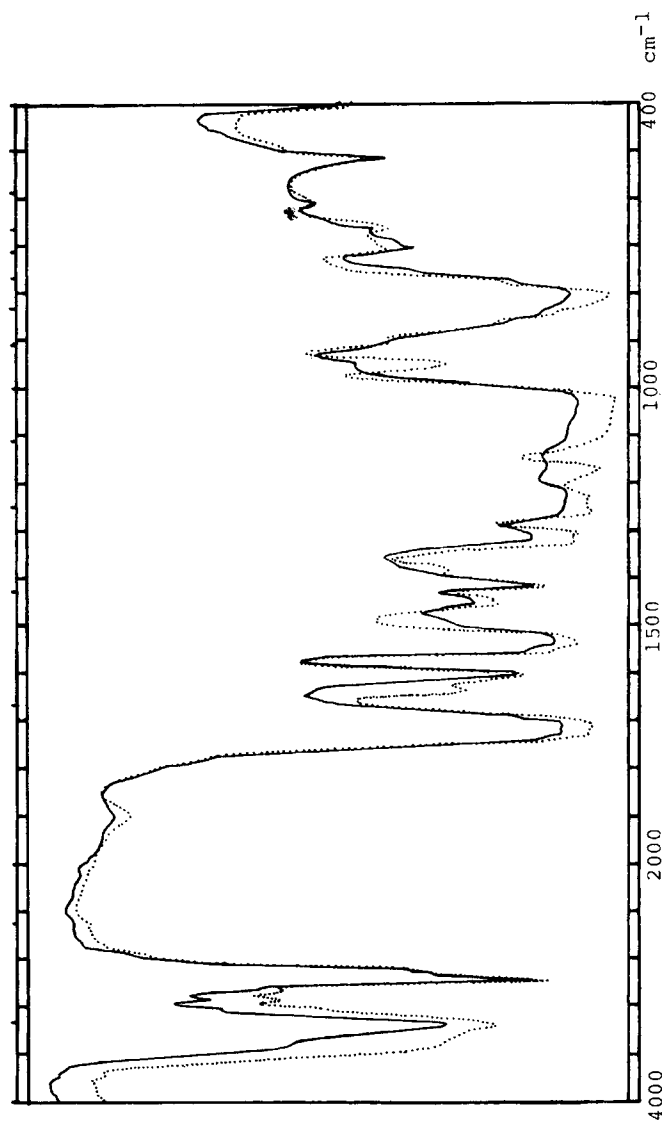


Fig. 2. Infrared spectra of pure resin with (—) and without (···) photocuring (PDMS1800/HDI).

TABLE I
Fundamental Properties of the PDMS Polyurethane Resin

	PDMS1800 /TDI /HEMA	PDMS1000 /TDI /HEMA	PDMS1800 /MDI /HEMA	PDMS1000 /MDI /HEMA	PDMS1800 /HDI /HEMA	PDMS1000 /HDI /HEMA
n_D^{25}	0.4912	0.4915	0.4909	0.4918	0.4904	0.4912
Color	Transparent and colorless		Transparent brown		Transparent and colorless	
Viscosity, cP	630	251	102	52	63	42
Solubility	(60% resin/40% acetone)					
Hardness (Shore D)	65	50	Acetone 95	THF 95	CHCl ₃ 95	CCl ₄ 90
	(dry film)					
\bar{M}_n	2020	1640	3600	1960	2500	2100
\bar{M}_w	2530	2810	6510	4450	5530	5830
MWD (\bar{M}_w/\bar{M}_n)	1.25	2.27	1.81	2.27	2.25	2.78
PDMS content (%)	75.9	63.7	71.4	58.1	76.4	64.3

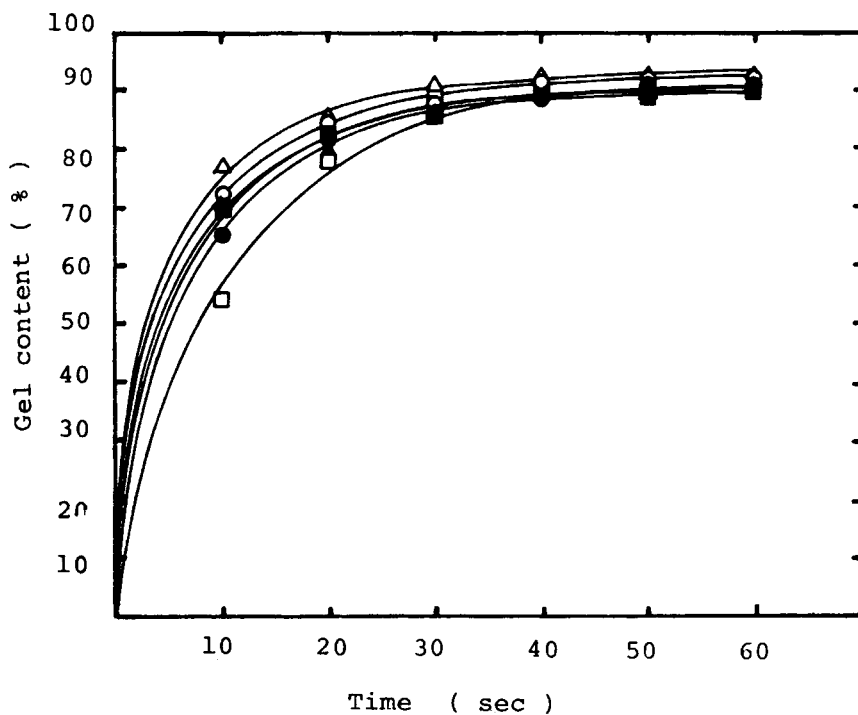


Fig. 3. Gel content of dry film as function of curing time: (▲): PDMS1000/MDI; (○): PDMS1000/TDI; (□): PDMS1000/HDI; (▲): PDMS1800/MDI; (●): PDMS1800/TDI; (■): PDMS1800/HDI.

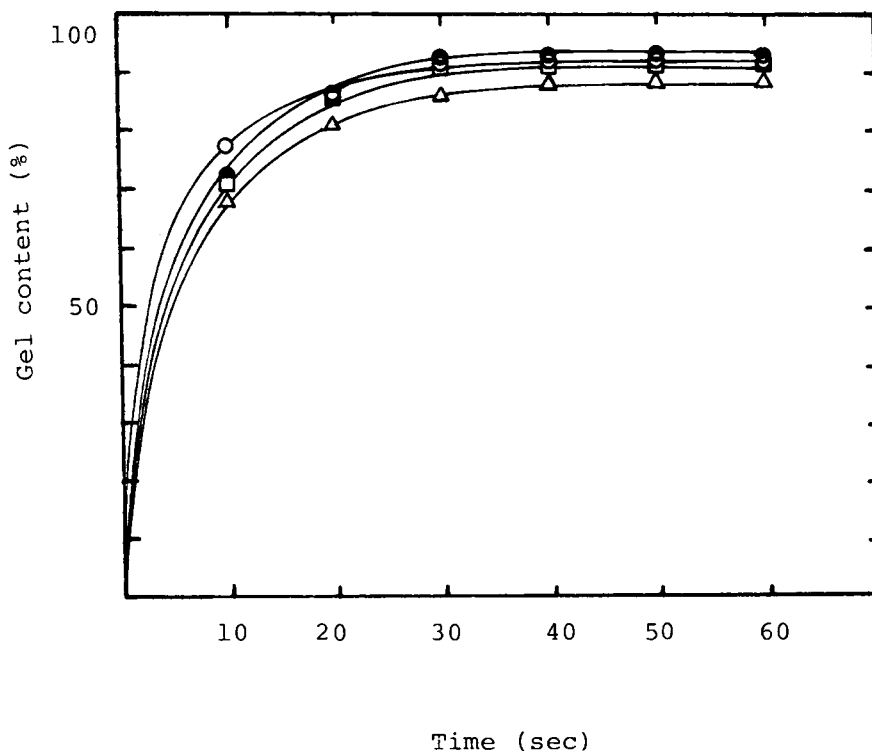


Fig. 4. Gel content of dry film as function of curing time (in PDMS1000/MDI system): (○): pure resin; (●): 25% TMPTA; (△): 25% SR395; (□): 25% SR238.

Thermal Properties

The thermogravimetric analysis of UV-cured resin is shown in Figures 5 and 6. Figure 5 shows that in all three systems, either thermal decomposition temperature or residues followed the tendency: MDI > TDI > HDI, when possessing the same PDMS molecular weight. This can be attributed to the ratio of hard segments within these resins. From these measurements, we find that the resin with higher PDMS molecular weight possesses a higher thermal decomposition temperature. All resins exhibited excellent thermal stability; all the thermal decomposition temperatures were about 280°C even though the resin had been mixed with various reactive diluents as shown in Figure 6. This might be at least partially due to the fairly strong silicone-oxygen bond.¹⁰ This bond has an energy of dissociation of 108 Kcal/mol as compared to 85.5 Kcal/mol for a C—C bond. The strong Si—O bond also results in chemical inertness and incompatibility with most organic materials, but siloxane polymers can also resist sunlight, weathering, ozone and, in general, conditions which would degrade most organic elastomers.

Mechanical Properties

The tensile properties of UV-cured films are given in Figures 7 to 10. Figures 7 and 8 show that the stress at break and Young's modulus gradually

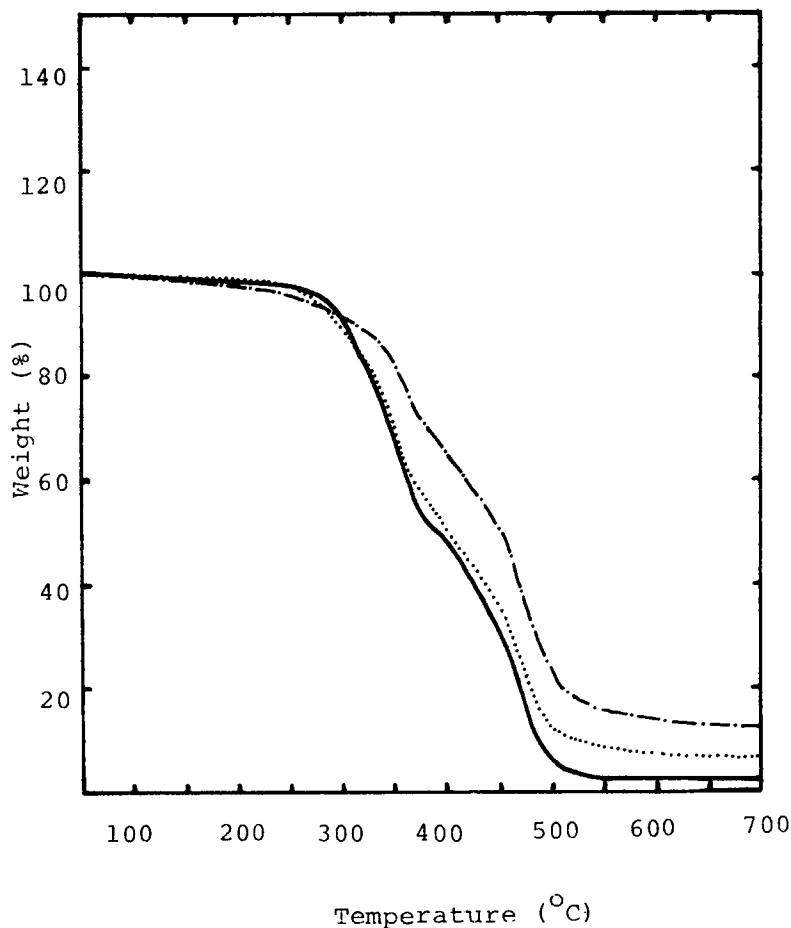


Fig. 5. Thermal decomposition analysis of dry film in various diisocyanate series: (···): PDMS1000/TDI; (—): PDMS1000/HDI; (-·-·): PDMS1000/MDI.

increased toward a constant with the increase in irradiation time whereas the elongation at break decayed to a near equilibrium value as shown in Figure 9. The behavior exhibited in the above figures was attributed to the fact that the photocrosslinking seemed to be complete and to acquire a stable property after about 20 s of photocuring time.

As a premise, PDMS chains exhibit weak mechanical properties because of the higher mobility of backbone. The mechanical strength of dry films, therefore, corresponds approximately to the ratio of hard segments within these materials. As given in Figures 7 and 8, both the tensile strength and Young's modulus tended to maintain the following order: MDI > TDI > HDI. Furthermore, the resins with higher PDMS molecular weight in the same diisocyanate system exhibit weaker mechanical strength because of their lower ratios of hard segments. However, the HDI series, which possessed a higher ratio of soft PDMS segment, and the resin with higher PDMS molecular weight gave a higher elongation at break as shown in Figure 9.

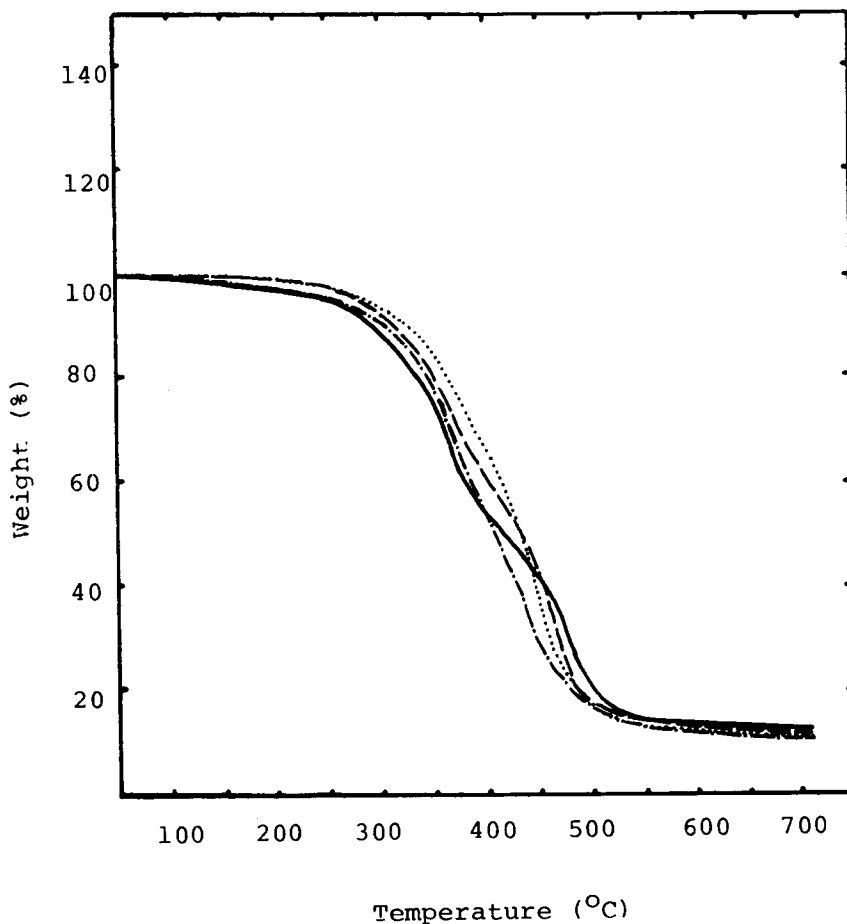


Fig. 6. Thermal decomposition analysis of dry film with various reactive diluent (in PDMS1000/MDI system): (—): pure resin; (···): 25% TMPTA; (-·-): 25% SR395; (- -): 25% SR238.

In the MDI/diluent system, given in Figure 10, the effect of reactive diluents which were used to improve the chemical properties of dry films followed the order:

$$\text{TMPTA} > \text{SR238} > \text{SR395}$$

This phenomenon was also attributed to the longer aliphatic chain and the lower content of unsaturated double bond within diluent SR238 and SR395. The unsaturated double bond (or acrylate) content of reactive diluents are as follows:

$$\text{TMPTA} : \text{SR238} : \text{SR395} = 3 : 2 : 1$$

Dielectrical Properties

From Figure 11 we find that the dielectric insulating properties follow the order:

$$\text{HDI} > \text{TDI} > \text{MDI}$$

when these resins were made with the same PDMS molecular weight. The

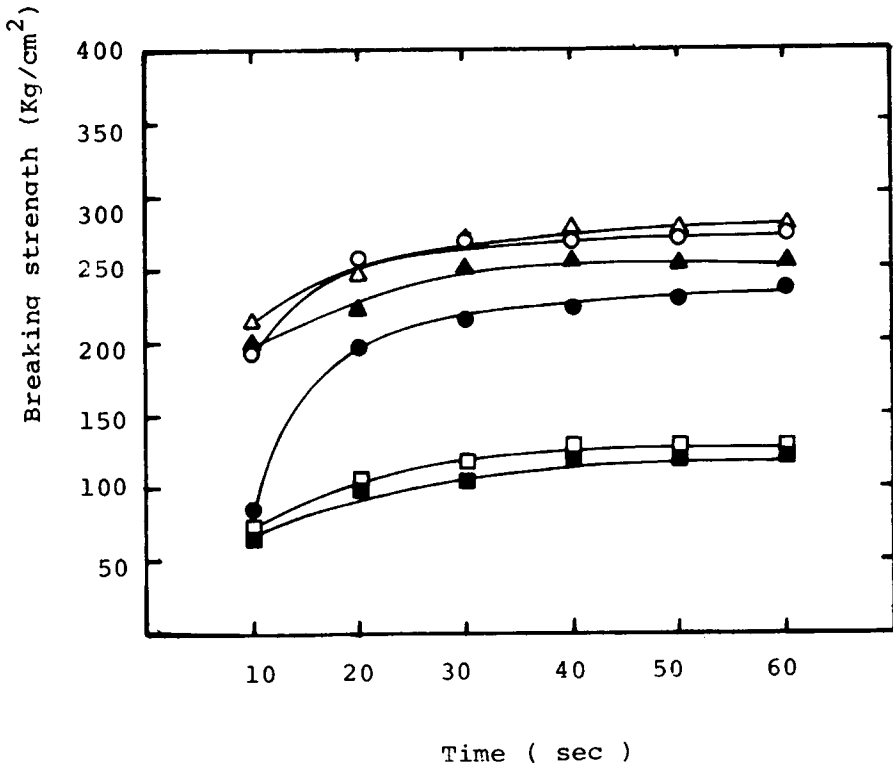


Fig. 7. Breaking strength of the dry film as function of irradiation time: (△): PDMS1000/MDI; (○): PDMS1000/TDI; (□): PDMS1000/HDI; (▲): PDMS1800/MDI; (●): PDMS1800/TDI; (■): PDMS1800/HDI.

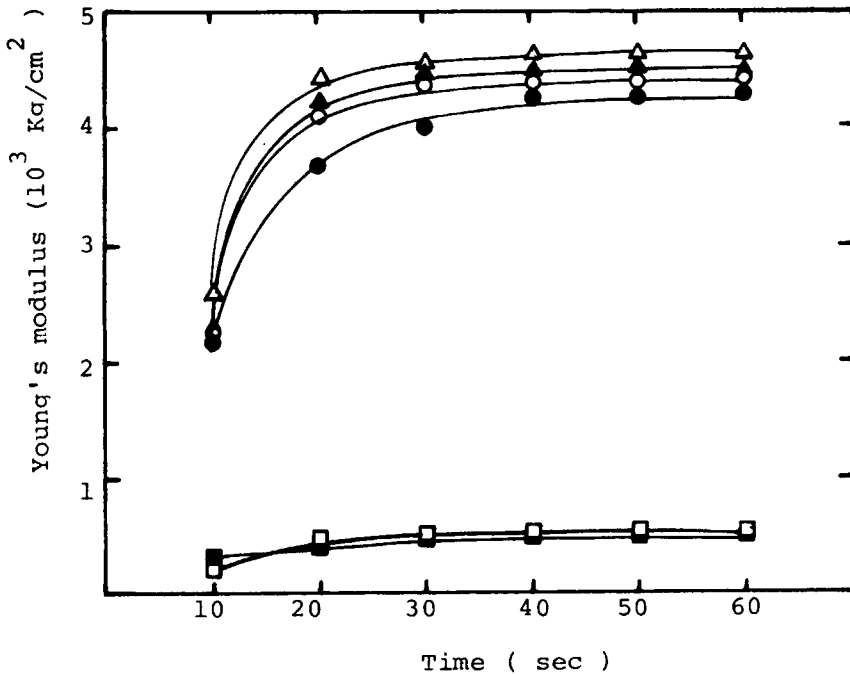


Fig. 8. Young's modulus of the dry film as function of photocuring time: (△): PDMS1000/MDI; (○): PDMS1000/TDI; (□): PDMS1000/HDI; (▲): PDMS1800/MDI; (●): PDMS1800/TDI; (■): PDMS1800/HDI.

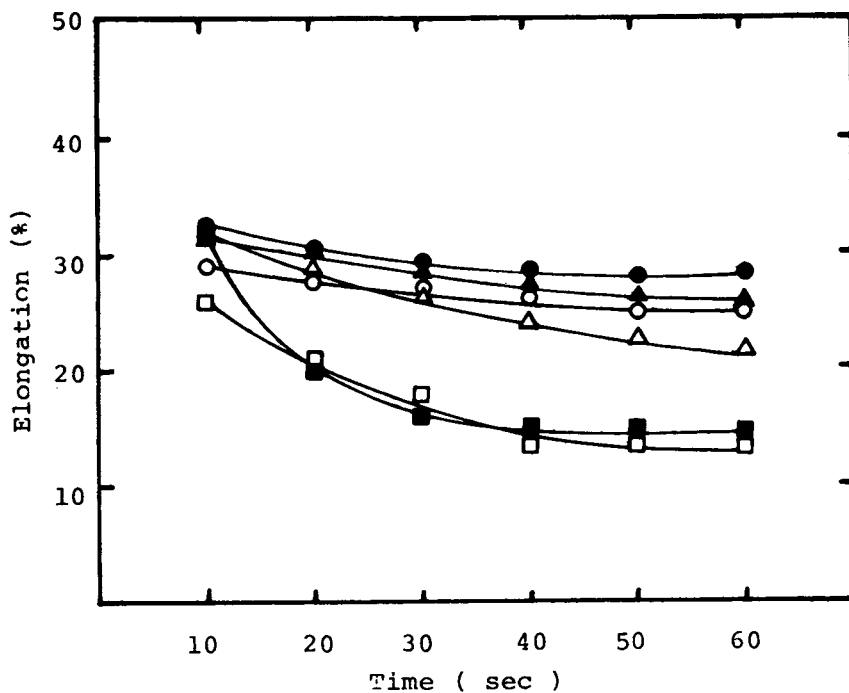


Fig. 9. Elongation of dry film at breaking point as function of photocuring time: (Δ): PDMS1000/MDI; (○): PDMS1000/TDI; (□): PDMS1000/HDI; (▲): PDMS1800/MDI; (●): PDMS1800/TDI; (■): PDMS1800/HDI.

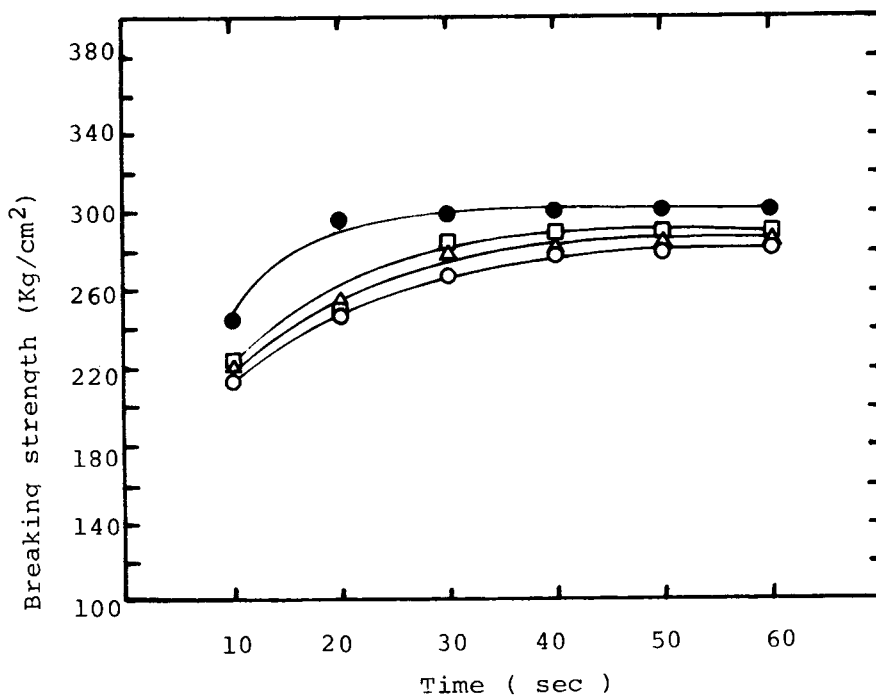


Fig. 10. Breaking strength of dry film as function of irradiation time (in PDMS1000/MDI system): (○): pure resin; (●): 25% TMPTA; (Δ): 25% SR395; (□): 25% SR238.

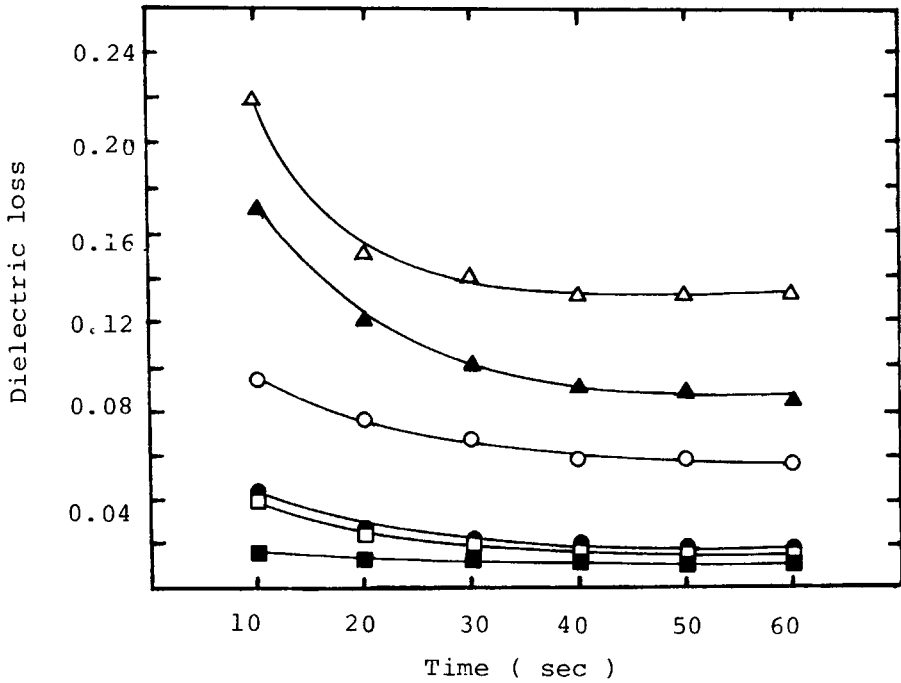


Fig. 11. Dielectric loss of dry film as function of photocuring time: (Δ): PDMS1000/MDI; (\circ): PDMS1000/TDI; (\square): PDMS1000/HDI; (\blacktriangle): PDMS1800/MDI; (\bullet): PDMS1800/TDI; (\blacksquare): PDMS1800/HDI.

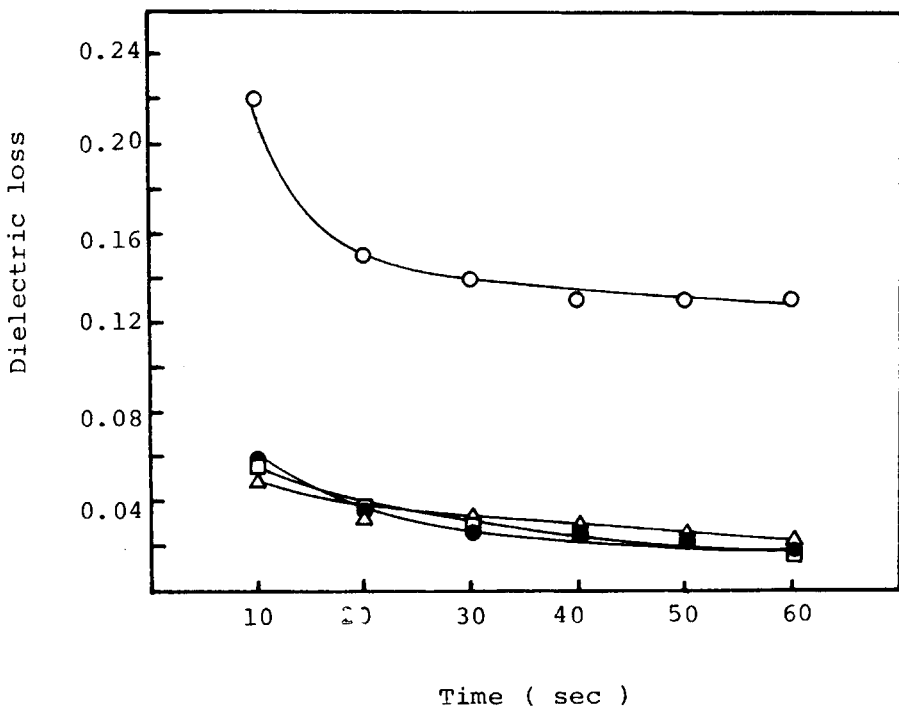


Fig. 12. Dielectric loss of dry film as function of photocuring time (in PDMS1000/MDI system): (\circ): pure resin; (\bullet): 25% TMPTA; (Δ): 25% SR395; (\square): 25% SR238.

sequence was related to the ratios of PDMS soft segments which exhibited excellent dielectric properties. The HDI series therefore suffered the lowest dielectric loss.

Similarly, we also find that the resin with a higher PDMS molecular weight in the same diisocyanate series would prohibit a higher volume resistivity and lower $\tan \delta$ or dielectric loss.

Generally speaking, this kind of material with insulated PDMS would exhibit a higher volume resistivity but a lower dielectric constant and $\tan \delta$ value, that is, a higher electrical insulation than the other polyurethanes.

The dielectric properties of the MDI/diluent system are shown in Figure 12. All the added reactive diluents could improve the dielectric insulating properties of UV-cured films.

TABLE II
Coating Test of MDI/PDMS1000 on Various Matrices

Test items	Matrices				
	Steel	Glass	Wood	Aluminum	PS
Irradiation time(s)	30	30	30	30	30
Film thickness (μm)	25	30	30	28	32
Adhesion test	OK	OK	OK	OK	OK
Hardness (pencil)	3H	3H	3H	3H	3H
Impact resistance	OK	—	OK	OK	OK
Extension test	OK	—	—	OK	—
Flexibility test	OK	—	—	OK	—
Chemical resistance					
1 HCl 5%	OK	OK	OK	OK	OK
2 NaOH 5%	OK	OK	OK	—	OK
3 NaCl 5%	OK	OK	OK	OK	OK
4 CH ₃ COOH 3%	OK	OK	OK	OK	OK
5 CH ₃ OH	X	X	X	X	X
Water resistance	OK	OK	OK	OK	OK
Detergent resistance	OK	OK	OK	OK	OK

TABLE III
Coating Test of HDI/PDMS1000 on Various Matrices

Test items	Matrices				
	Steel	Glass	Wood	Aluminum	PS
Irradiation time(s)	30	30	30	30	30
Film thickness (μm)	26	31	32	30	28
Adhesion test	OK	OK	OK	OK	OK
Hardness (pencil)	2H	2H	2H	2H	2H
Impact resistance	OK	—	OK	OK	OK
Extension test	OK	—	—	OK	—
Flexibility test	OK	—	—	OK	—
Chemical resistance					
1 HCl 5%	OK	OK	OK	OK	OK
2 NaOH 5%	OK	OK	OK	—	OK
3 NaCl 5%	OK	OK	OK	OK	OK
4 CH ₃ COOH 3%	OK	OK	OK	OK	OK
5 CH ₃ OH	X	X	X	X	X
Water resistance	OK	OK	OK	OK	OK
Detergent resistance	OK	OK	OK	OK	OK

Coating Properties

The synthesized resin cast on various substrates, such as steel, glass, aluminum, wood, and plastics (PS), which had been subject to a surface treatment before casting, was measured for coating properties. Tables II and III list the test results of various coating properties including scratch hardness, adhesive properties, impact resistance, extensibility, flexibility, and chemical resistance. The PDMS polyurethane resin exhibited an excellent coating property in the various matrixes regardless of the adhesion or impact test. In addition, the Si—O—Si structure of PDMS is similar to the component SiO₂ of glass, promoting good adhesion between resin and matrix. Thus, we also obtain superior coating properties on glass.

CONCLUSION

The PDMS-polyurethane UV-curable resins synthesized by hydroxy-terminated polydimethylsiloxane (PDMS) and various diisocyanates were transparent liquid oligomers. The synthesis reaction was carried out in a nonsolvent system. All the UV-cured films exhibit excellent thermal stability and possess thermal decomposition temperature over 280°C. In addition, the resin with a higher PDMS molecular weight possesses higher volume resistivity. Lower $\tan \delta$ values and dielectric losses are attributed to the insulation character of PDMS materials. Moreover, the dielectric insulating properties of dry films tend to the following order: HDI series > TDI series > MDI series because of the greater PDMS content.

Because the PDMS chain possesses weaker mechanical properties, both the tensile strength and Young's modulus of UV-cured films tended to have the following order: MDI > TDI > HDI. Furthermore, the resin with a higher PDMS molecular weight in the same diisocyanate system exhibited a weaker mechanical strength because of their lower ratio of hard segments.

The mixed reactive diluents were shown to reduce the viscosity of the whole system and promote processability, as well as improve the surface gloss of dry films, and their transparency and mechanical properties, etc. The tensile strength of dry films was affected directly by the compatibility of the reactive monomer with the soft and rigid segments of resin and the functionality (unsaturated double bond) of diluents.

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