

Synthesis and Characterization of New Functional Poly(urethane-imide) Crosslinked Networks

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Received 11 March 2005; accepted 15 July 2005

DOI 10.1002/app.22678

Published online 9 January 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To synthesize new functional poly(urethane-imide) crosslinked networks, soluble polyimide from 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride, 4,4'-oxydianiline, and maleic anhydride and polyurethane prepolymer from polycaprolactone diol, tolylene 2,4-diisocyanate and hydroxyl ethyl acrylate were prepared. Poly(urethane-imide) thin films were finally prepared by the reaction between maleimide end-capped soluble polyimide (PI) and acrylate end-capped polyurethane (PU). The effect of polyurethane content on dielectric constant, residual stress, morphology, thermal property, and mechanical property was studied by FTIR, prism coupler, Thin Film Stress Analyzer (TFSA), XRD, TGA, DMTA, and Nano-indentation. Dielectric constant of poly(urethane-imide) thin films (2.39–2.45) was lower than that of pure polyimide (2.46). Especially, poly(urethane-imide) thin films with 50% of PU showed lower dielectric constant than other poly(urethane-

imide) thin films did. Lower residual stress and slope in cooling curve were achieved in higher PU content. Compared to typical polyurethane, poly(urethane-imide) thin films exhibited better thermal stability due to the presence of the imide groups. The glass transition temperature, modulus, and hardness decreased with increase in the flexible PU content even though elongation and thermal expansion coefficient increased. Finally, poly(urethane-imide) thin films with low residual stress and dielectric constant, which are strongly affected by the morphological structure, chain mobility, and modulus, can be suggested to apply for electronic devices by variation of PU. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 113–123, 2006

Key words: polyimide; polyurethane; poly(urethane-imide) thin films; dielectric constant; residual stress; morphology; modulus

INTRODUCTION

Polyurethanes (PUs) are highly elastic and linear segmented polymers with well defined micro-phase morphology. The need for PUs steadily increased ever since it was invented, because of its high abrasion, chemical resistant, flexibility, and good mechanical strength. Moreover, it forms various materials ranging from stiff thermoplastics to rigid thermosets just by changing the monomer combinations and additives. Despite the merits of this versatile polymer, its thermal stability is a point of concern, which restricts its application above 150°C, where its acceptable mechanical properties vanish.¹ Since many engineering applications require operating temperature above 150°C, the thermal stability of PUs has to be improved over 150°C. Many approaches have been adopted by research groups to increase the useful temperature range of PUs, of which, introducing thermally stable

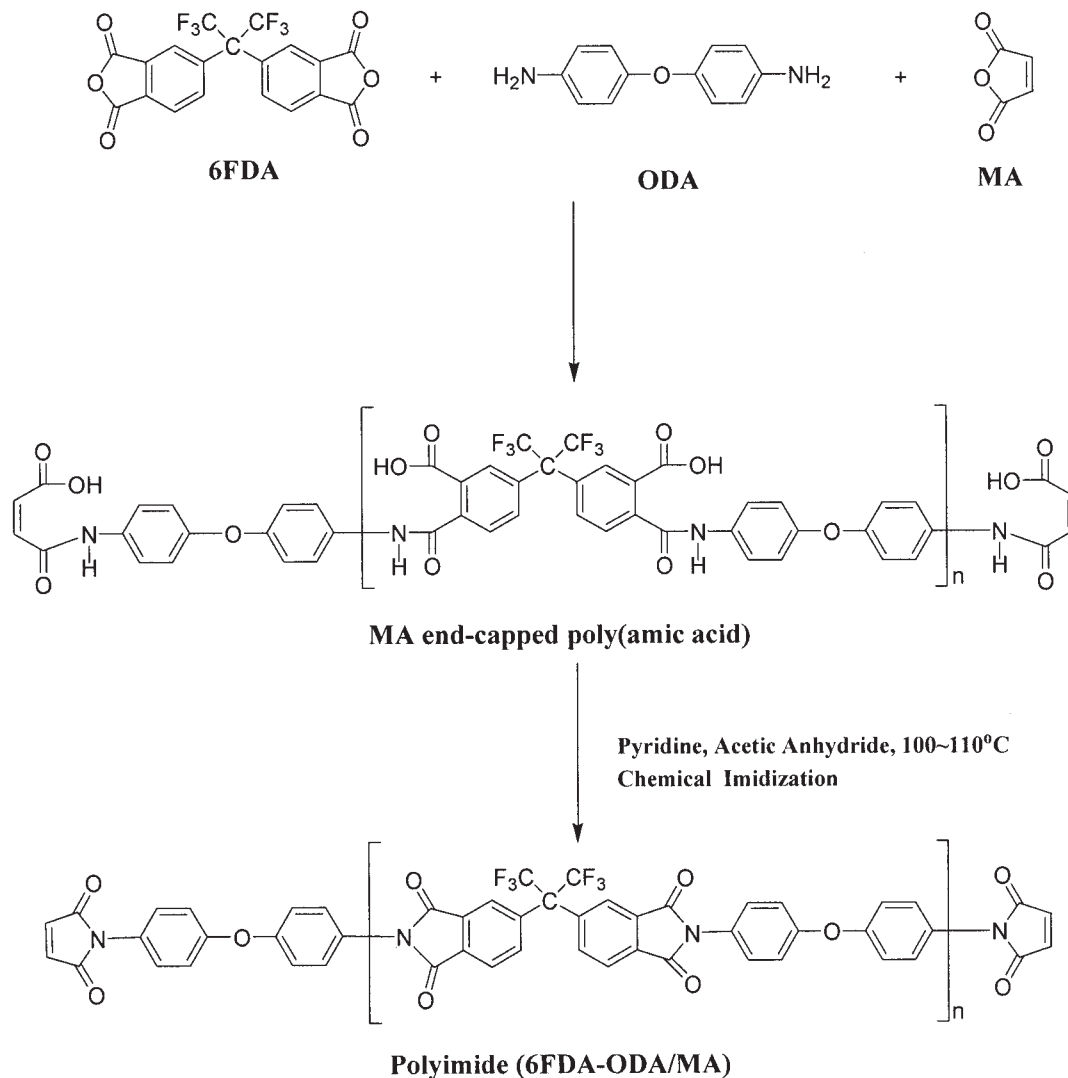
heterocyclic groups into PU chain has proved to be an effective and convenient route.

Polyimides (PIs), a heterocyclic polymer with outstanding thermal, mechanical, and electrical properties, are dominant in many engineering applications.² All these properties are due to its rigid backbone, but it makes the polymer insoluble, infusible, and difficult to process, and the resulting films are brittle in nature. When PIs and PUs are combined, they can show synergic properties and the final materials can have desirable properties of both the polymers. PIs and PUs could be combined in many ways and the most adopted method is preparing copolymers.

Poly(urethane-imide) is prepared by many methods like reacting isocyanate end-capped PU prepolymer with dianhydride,^{3,4} reacting diols having built-in imide moiety^{5,6}, and reacting 4-methyl-1,3-phenylene bis(2-furanylcarbamate) with various bismaleimides through a Diels–Alder (DA) reaction.^{7,8} These polymers are primarily linear in structure and may result in poor solvent resistant properties. As a way to enhance the solvent and make it heat-resistant, crosslinked structures are proposed and Takeichi and coworkers prepared a number of crosslinked polyimides and copolyimides through different methodologies.^{9–12}

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Contract grant sponsor: Ministry of Science and Technology of Korea (National Research Laboratory Program).



Scheme 1 Synthesis of soluble polyimide (6FDA-ODA/MA).

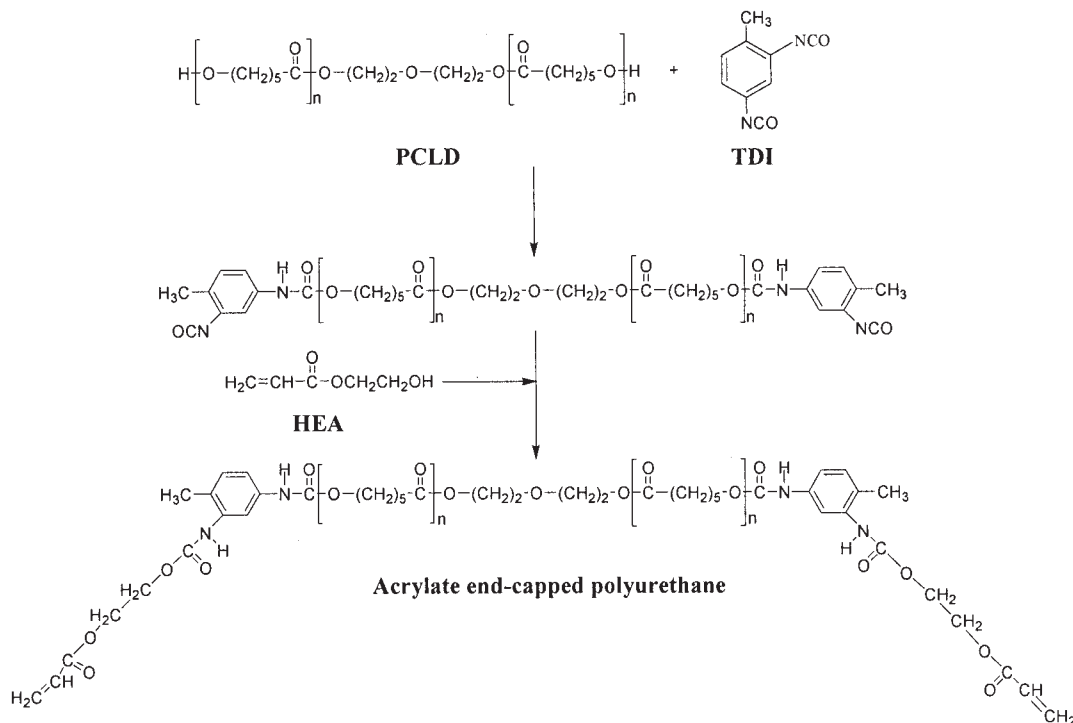
The reported methods of preparing crosslinked structure use the reaction of NCO-terminated polyurethanes with poly(amic acid) precursors,⁹ the preparation of polyimides with hydroxyl groups using diamines with hydroxyl groups¹⁰, and dianhydride having hydroxyl groups¹¹ then reacting these reactive polyimides with NCO-terminated polyurethanes. In this paper, we report a novel method of preparing poly(urethane-imide) crosslinked networks, in which the maleimide end-capped polyimide was reacted with acrylate end-capped polyurethanes. The advantage of this method is that it involves radical reactions, which are fast and convenient, and even energy saving UV curing methods can be employed to effect crosslinking. Also, unlike blends, since the two polymers are chemically reacted, the phase separation has not occurred. Moreover, the plastic-elastic balance can be easily adjusted by varying the weight ratio of the two polymers.

In this study, a series of poly(urethane-imide) crosslinked networks was prepared by novel method by varying the weight ratio of the two polymers. The effect of PU content on the dielectric constant, residual stress behavior, morphology, thermal property, and mechanical property was investigated. The measured residual stress was interpreted on the basis of the morphological structure, chain mobility, and modulus.

EXPERIMENTAL

Materials and purification

2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane (6FDA; CHRISKEV 99.5%) was purified by sublimation under vacuum. 4,4'-Oxydianiline (ODA; Aldrich 97%) was purified by recrystallization from ethanol and maleic anhydride (MA; Aldrich 99%) was used as



Scheme 2 Synthesis of acrylate end-capped polyurethane prepolymer.

received. *N*-Methyl-2-pyrrolidinone (NMP; Lancaster 99%) was distilled under reduced pressure. Polycaprolactone diol of molecular weight 2000 (PCLD; Aldrich) was used after drying at 105°C under vacuum for 4 h. Toluene 2,4-diisocyanate (TDI; Aldrich 95%), hydroxy ethyl acrylate (HEA; Aldrich 96%), dibutyltin dilaurate (DBTDL; Aldrich 95%) and 4,4'-azobis(4-cyano-valeric acid) (ACVA; Aldrich >75%) were used as received. All other chemicals were analytical grades and were used as received. Other organic solvents were obtained commercially and used as received.

Synthesis of soluble polyimide

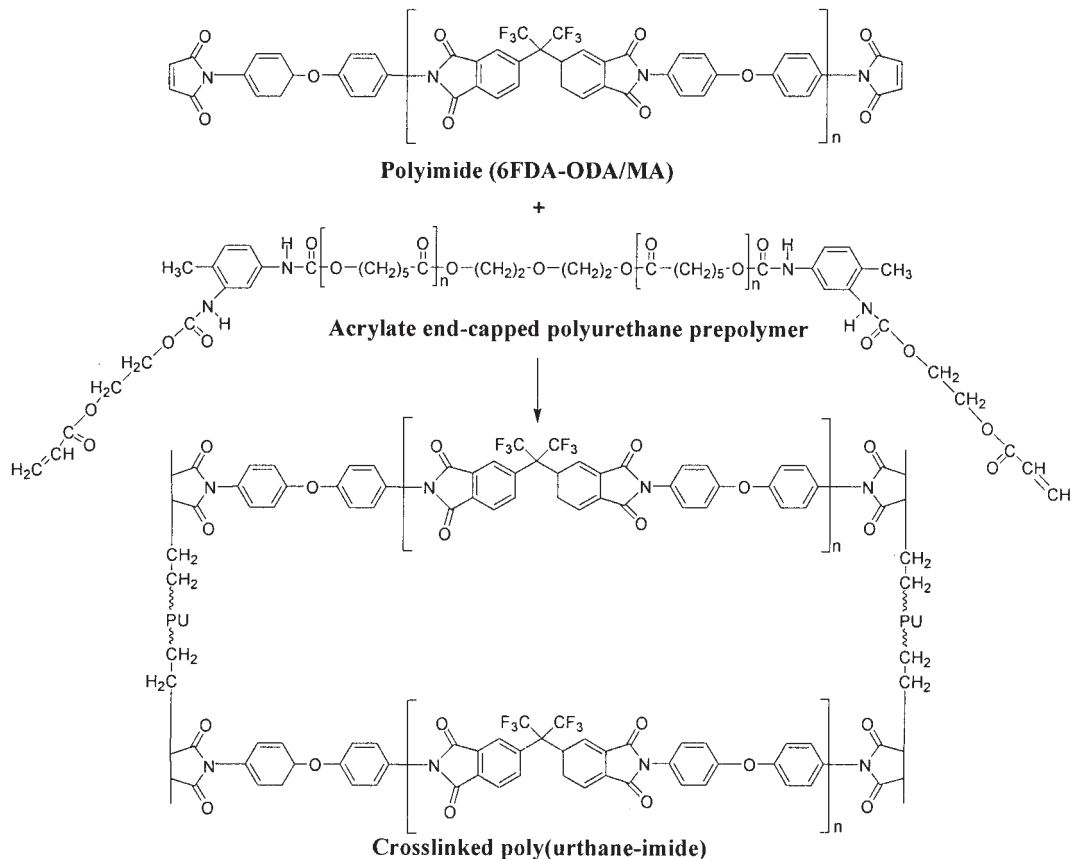
ODA (4.4 mmol) and 12 mL NMP were placed into a flask equipped with a nitrogen inlet and a magnetic stirrer and then stirred until clear solutions were obtained. 6FDA (4 mmol) and 3 mL NMP were added to the solution of diamine. After reacting for 12 h at room temperature, 0.8 mmol of MA was added and reacted for further 12 h. Then the mixture of acetic anhydride and pyridine (five times the mole of dianhydride) were added in the obtained brown viscous solution of poly(amic acid)s (PAAs) and heated at 100–110°C for 12 h. All the reactions were performed under N₂ atmosphere. The obtained polyimide was precipitated in excess amount of deionized water and the resulting precipitate was washed thoroughly in methanol, filtered and dried under vacuum at 80°C. The synthesis route is given as Scheme 1.

Synthesis of acrylate end-capped polyurethane

PCLD 2000 (5 mmol) was added dropwise to TDI (10 mmol) in a 100-mL three-neck round bottom flask at 40°C in N₂ atmosphere for 1 h. The temperature was then raised to 80°C and the reaction was allowed to proceed till the isocyanate content reached half of the initial value (as determined by dibutylamine titration). The temperature was reduced to 60°C and HEA (10 mmol) was added dropwise, then 0.01 g of DBTDL catalyst was added and the reaction was allowed to go to completion as confirmed by the absence of isocyanate peak in the FTIR spectrum. The synthesis route is given as Scheme 2.

Synthesis of poly(urethane-imide) thin films

For the preparation of poly(urethane-imide)s, the ratios of used polyimide and polyurethane (PI/PU) were 100/0, 90/10, 70/30, and 50/50 respectively. Required quantity of polyimide and NMP at about 10–30 wt % were weighed into a 50 mL conical flask and stirred until the polyimide was completely dissolved in NMP. The required amount of acrylate end-capped polyurethane was added and stirred for homogeneity. 4,4'-Azobis(4-cyano-valeric acid) was added about 3 wt %. The poly(urethane-imide) thin films for residual stress and prism coupler were cast on Si (100) wafer by spin coater (ASS 301 series, Japan) in which the thickness of the films can be precisely



Scheme 3 Curing process of poly(urethane-imide).

controlled. The cast films were cured at 80°C for 4 h, at 120°C for 6 h, and at 180°C for 3 h. The cured poly(urethane-imide) thin films were immersed in deionized water to release the films from the wafer and dried in vacuum oven at 80°C for 5 h. Before and after measurement, the film thickness was measured using a surface profiler (Tencor Instruments Co., Model AS500). The synthesis route is given as Scheme 3.

Measurements

FTIR spectrum was obtained using Excalibur series (DIGILAB Co.) instrument in the range of 400–4000 cm^{-1} using ATR accessory. TGA thermograms were obtained from Thermogravimetric Analyzer (TA Instruments Co., New Castle, DE) in the temperature range of 25–800°C at a heating rate of 10°C/min in N_2 atmosphere. The Differential Scanning Calorimeter (TA Instruments, DSC Q1000) measurements were applied from 30 to 300°C at a heating rate of 10°C/min. The dynamic mechanical thermal analysis (DMTA) measurements were performed with a PL series (Polymer Laboratories Co., Amherst, MA) from 50 to 200°C at a heating rate of 5°C/min and at a frequency of 1 Hz.

The residual stress was measured by using TFSA (Fig. 1).^{13–16} The curvatures of Si wafer with and without films were measured at room temperature using He–Ne laser beam in the temperature range of 30–200°C. The residual stress was calculated from the radii of the wafer curvatures measured before and after the film deposition using the following eq. (1).

$$\sigma = \frac{1}{6} \frac{E_s}{(1 - \nu_s)} \frac{t_s^2}{t_f} \left(\frac{1}{R_2} - \frac{1}{R_1} \right) \quad (1)$$

Where, σ is the residual stress in the poly(urethane-imide) thin film. The subscripts, f and s denote the poly(urethane-imide) thin film and the substrate. E , ν , and t are Young's modulus, Poisson's ratio, and the thickness respectively. R_1 and R_2 are the wafer curvatures measured before and after the film deposition. For Si (100) wafer, $E_s/(1 - \nu_s)$ is 180,500 MPa.

The dielectric property of poly(urethane-imide) thin films is studied via the optical method and capacitance method. For the optical dielectric constant, the out-of-plane and in-plane refractive indexes of poly(urethane-imide) thin films were measured with a prism coupler (Metricron, model 2010) equipped with a He–Ne laser light source (wave length = 632.8 nm)

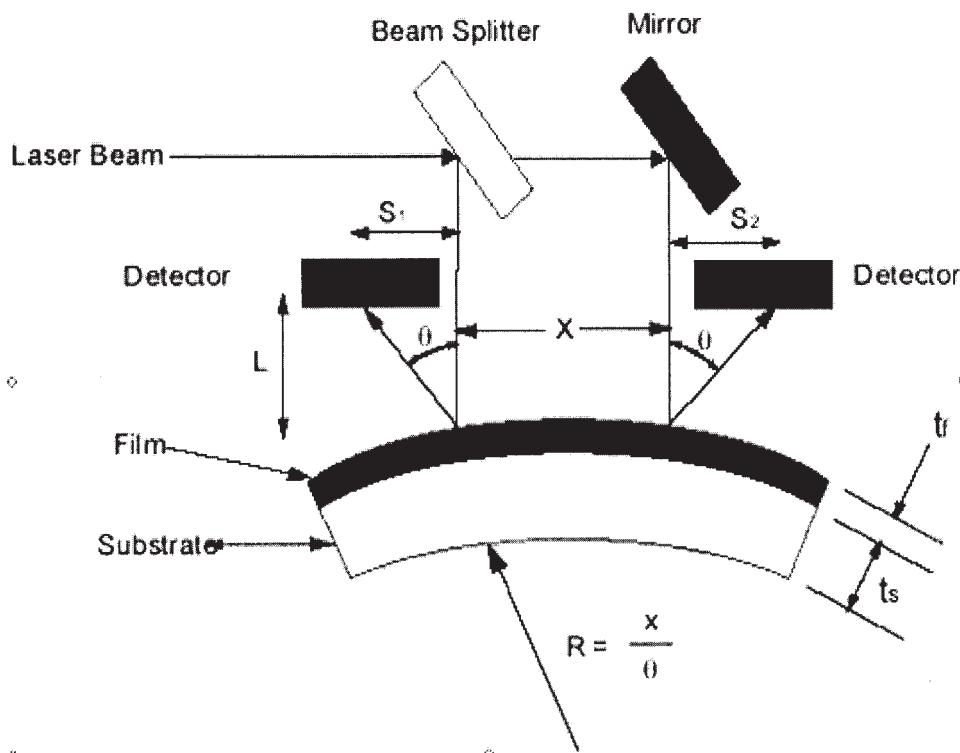


Figure 1 Optical setup for the residual stress measurement in TFSA.

and controlled by a computer. Measurements of the refractive indexes were carried out in transverse electric (TE) and transverse magnetic (TM) modes with the appropriate polarization of the incident laser beam, as described elsewhere.^{17,18} The TE measurement in which the electric field was in the film plane provided the in-plane refractive index (n_{TE}), whereas the TM measurement in which the electric field was out-of-plane gave the out-of-plane refractive index (n_{TM}). Both in-plane and out-of-plane refractive indices were used to compute the three-dimensional average refractive index, as given in eq. (2).

$$n_{av} = (2n_{xy} + n_z)/3 \quad (2)$$

In capacitance methods, the dielectric constant of poly(urethane-imide) thin films was measured at room temperature and 1 kHz with a Film Dielectric Property Analyzer (FDPA; Fluke PM6304).

For the morphological structure of the poly(urethane-imide) thin films, WAXD patterns were ob-

tained with a Rigaku horizontal X-ray diffractometer (D/Max-2500H). The diffractometer was set up for the reflection mode (i.e., reflections from lattice planes parallel to the film surface) with a curved graphite monochromator in the diffracted beam. The Cu K α radiation source ($\lambda = 1.54 \text{ \AA}$) was operated at 40 kV and 40 mA. All the WAXD measurements were carried out in the $\theta/2\theta$ mode. The 2θ scan data were collected from 3 to 60° at 0.02° intervals with a scan speed of 0.4°/min. The measured X-ray diffraction intensities were corrected for the background.

A nano-indenter (MTS XP System) was used to measure the mechanical properties of the polyimide thin films. A Berkovich (three-faced-pyramid) indenter was used in this study. Multiple indentations were made at different locations of the film surface at a fixed penetration depth. At different locations, the load-displacement curve was recorded, from which the effective modulus and hardness could be calculated with standard formulas. In addition, the actual

TABLE I
Solubility of Soluble Polyimide (6FDA-ODA/MA)

Polyimide	Solvent					
	NMP	<i>m</i> -Cresol	THF	acetone	MC	Methanol
6FDA-ODA/MA	o	o	o	×	o	o

o: soluble, ×: insoluble.

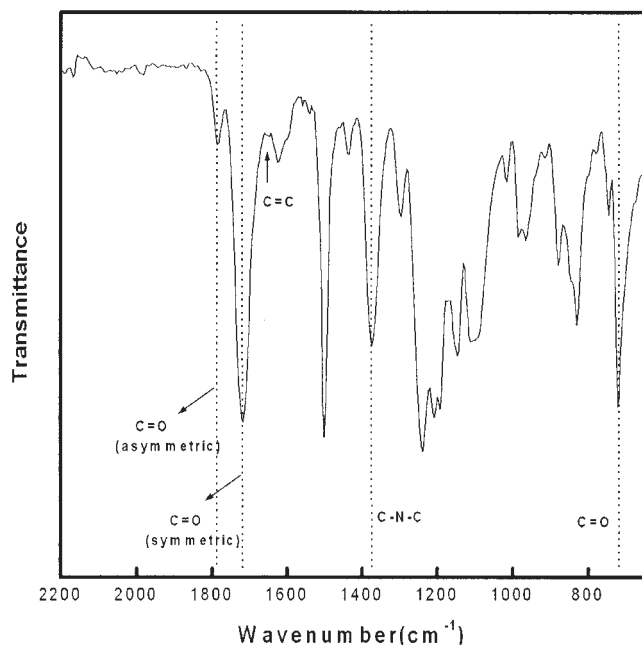


Figure 2 FTIR spectrum of polyimide (6FDA-ODA/MA).

plastic (permanent) deformation was determined at the end of each loading cycle.

RESULTS AND DISCUSSION

Solubility

Solubility characteristics of MA end-capped polyimide in common organic solvents like NMP, *m*-cresol, tetrahydrofuran (THF), acetone, methylene chloride (MC), and methanol were evaluated and the results are compiled in Table I. The polymer solubility was evaluated in 3 wt % of the solvent in room temperature for a period of 2 h. The polyimide was soluble in many solvents with the exception of acetone and methanol and hence it was possible to carry out further process with polyurethane. The increased solubility is due to the presence of bulky CF_3 groups in the dianhydride and the flexible ether linkage in the diamine. Moreover, this solubility of polyimide also can be due to the chemical imidization method, which reduces charge transfer interaction.¹⁹

FTIR spectrum

The completion of the imidization and crosslinking was confirmed by the FTIR and a spectrum of MA end-capped polyimide is given in Figure 2. The asymmetric and symmetric $>\text{C}=\text{O}$ stretching of MA end-capped polyimide are observed around 1780 and 1720 cm^{-1} . Also the C—N—C absorption at 1373 and 721 cm^{-1} (out of phase bending of imide ring) confirmed the formation of imides. The C=C stretching of MA is

observed around 1651 cm^{-1} . Figure 3 gives the spectrum of acrylate end-capped polyurethane. The FTIR spectra of acrylate end-capped polyurethane and cationomers show characteristic peaks due to urethane —NH at 3336 cm^{-1} . The $>\text{C}=\text{O}$ stretching and C—N—H absorption of urethane linkage are observed at 1720 and 1535 cm^{-1} . The C=C peak around 1635 cm^{-1} confirms the incorporation of HEA and the absence of NCO peak at 2260 cm^{-1} confirms the complete end-capping of HEA with PU. Figure 4 gives the FTIR spectrum of poly(urethane-imide) thin films. The absence of C=C stretching frequency (1635 and 1651 cm^{-1}) confirms the completion of crosslinking.

Dielectric property

The dielectric constants for the poly(urethane-imide) thin films were evaluated by optical method and capacitance method and the values are summarized in Table II. Using Maxwell relation, the dielectric constants by optical method were calculated from the refractive indexes of poly(urethane-imide) thin films in the TE and TM modes, which were obtained from prism coupler.^{17,18} For the comparison with dielectric property, the dielectric constant by optical method in the perpendicular direction of the film orientation was taken. In general, fluorine substitution reduces the refractive index and polarizability. The predominant among them is fluorine reduces the moisture absorption of the film and hence reduces the polarizability and refractive index. Then, fluorine by itself has low polarizability and low refractive index, hence when it replaces the highly polarizable C, N, O, and H, the resultant polarizability of the system get reduced. Be-

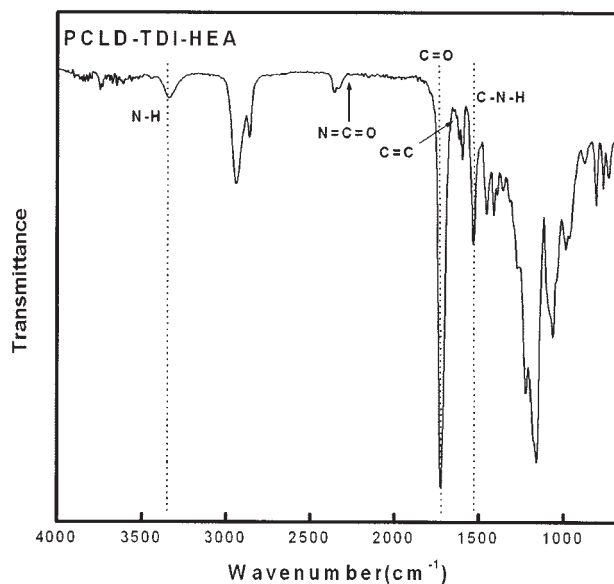


Figure 3 FTIR spectrum of HEA end-capped polyurethane prepolymer.

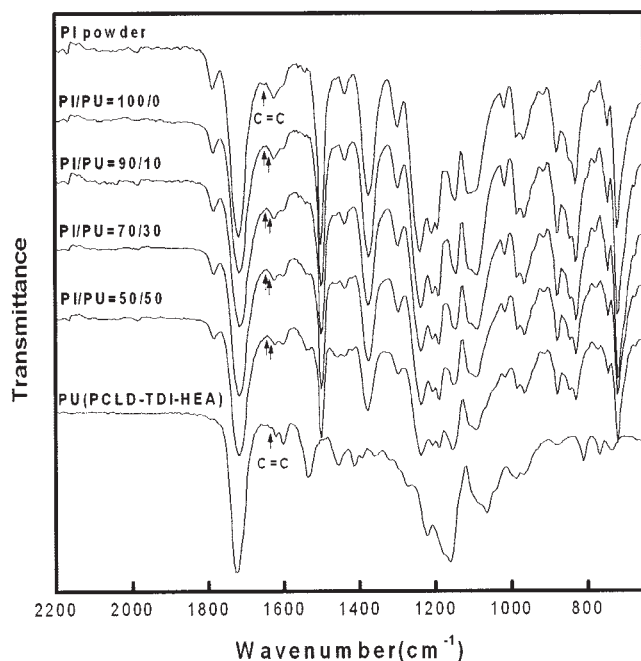


Figure 4 FTIR spectrum of poly(urethane-imide)s.

cause of its bigger size and fluorine–fluorine repulsion, it reduces the chain packing. This increases the free volume, which reduces the total number of polarizable atoms in a molar volume concerned and it also reduces the interchain electronic interactions.^{18,20,21} These reduce the polarizability of the whole system.

The dielectric constant for the poly(urethane-imide) thin films decreased in the order of PI/PU = 100/0 > PI/PU = 90/10 > PI/PU = 70/30 > PI/PU = 50/50. With increase in the amount of PU content, the dielectric constant of the poly(urethane-imide) thin films decreased. With increase in the amount of flexible polyurethane groups the polymer orientation was disrupted and the free volume was increased. These reduced the polarizability of the whole system. This result was observed in the trend by capacitance method. For all polymer thin films, the dielectric constants calculated by the optical method were lower than those measured by the capacitance method. This may be due to the difference in polarization according to the frequency range.

TABLE III
Residual Stress, Slope in Cooling Curve, and *d*-Spacing Values of Poly(urethane-imide) Thin Films

Poly(urethane-imide)	Residual stress (MPa)	Slope in cooling curve (MPa/°C)	<i>d</i> -spacing value ^a (Å)
PI/PU = 100/0	48	−0.194	5.42
PI/PU = 90/10	50	−0.281	5.14
PI/PU = 70/30	41	−0.297	4.67
PI/PU = 50/50	5	−0.038	4.43

^a calculated from the peak maximum of amorphous halo in the reflection WAXD pattern.

Residual stress behavior

All the poly(urethane-imide) thin films were made around 10 μm thick using spin coater and the exact thickness were measured by surface profiler. The residual stress of poly(urethane-imide) thin films at 30°C is listed in Table III. The slope of the cooling curve was found from the residual stress curves. The heating and cooling curves of poly(urethane-imide) thin films are given in Figure 5. The residual stress composed of two components; thermal stress and intrinsic stress.^{22,23} Generally thermal stress is considered as residual stress neglecting the small contribution of intrinsic stress. The thermal stress of the film (σ_t) can be calculated from the radius of the film curvature measured using the following eq. (3).

$$\sigma_t = (\alpha_f - \alpha_s)(T_f - T) \frac{E_f}{(1 - \nu_f)} \quad (3)$$

Where, α_f and α_s are the thermal expansion coefficients (TECs) of film and substrate respectively, and T_f is the final heating temperature (when T_f is over glass transition temperature of polymer films, T_f is regarded as glass transition temperature). The thermal stress is due to the mismatch of TECs of film and substrate. For all the poly(urethane-imide) thin films, the residual stress was measured by heating up to 200°C, annealing for 1 min, and cooling to 30°C. The slope of the cooling curve remains constant in all the experiments. It can be understood from the equation that the thermal stress depends upon the TECs of the film and the

TABLE II
Dielectric Properties of Poly(urethane-imide) Thin Films by Optical Method and Capacitance Method

Poly(urethane-imide)	Optical method, 474.1 THz				Capacitance method,
	n_{xy}	n_z	n_{ave}	ϵ'	1 kHz ϵ'
PI/PU = 100/0	1.5990	1.5693	1.5891	2.4627	3.6022
PI/PU = 90/10	1.5816	1.5667	1.5766	2.4545	3.4091
PI/PU = 70/30	1.5625	1.5554	1.5601	2.4193	3.3603
PI/PU = 50/50	1.5513	1.5465	1.5517	2.3917	3.1185

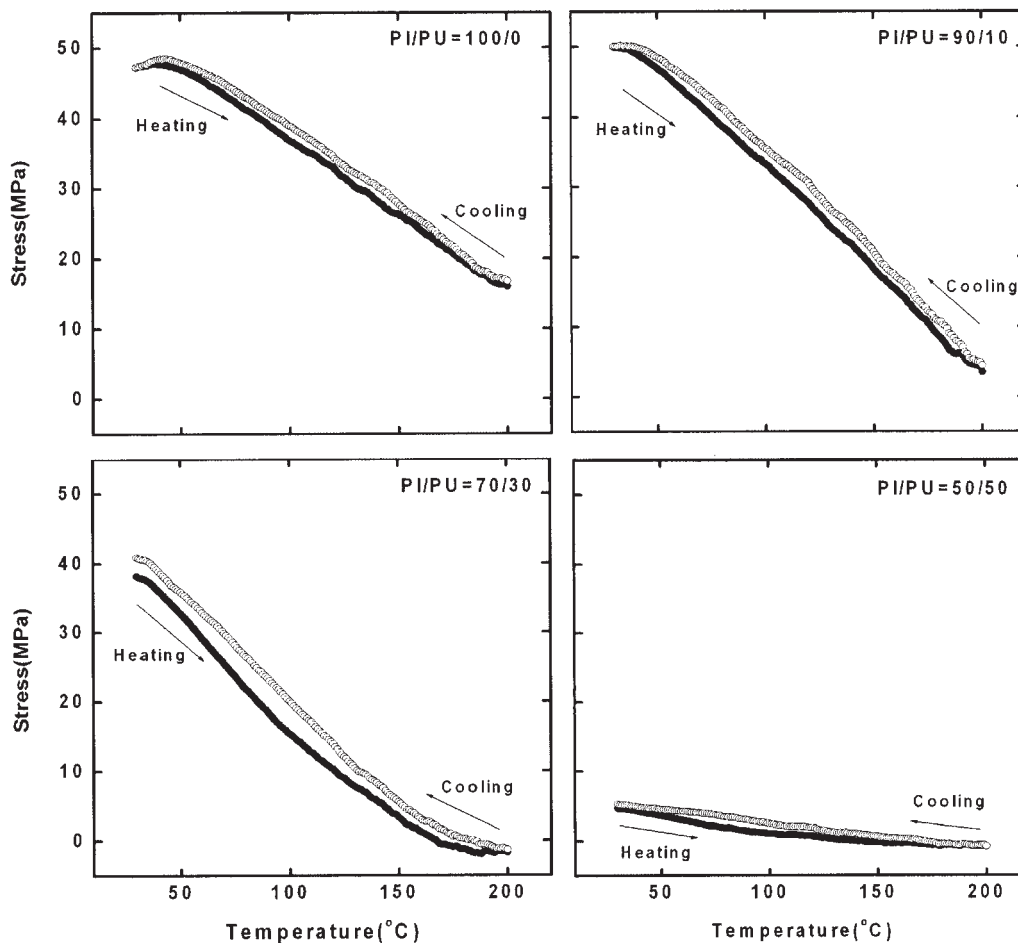


Figure 5 Residual stress curves of poly(urethane-imide)s.

substrate, Poisson's ratio ν , Young's modulus E , and process temperature. TEC of the substrate is 3 ppm, which remains constant and the Poisson's ratio of the poly(urethane-imide) thin films do not vary with temperature. Then the thermal stress depends on the modulus and TEC of the poly(urethane-imide) thin films. When temperature decreases, modulus increases slightly and TEC decreases slightly and that makes the term, $(\alpha_f - \alpha_s) \frac{E_f}{(1 - \nu_f)}$, almost constant and hence the slope of the cooling curve remains constant.^{14,24}

For all the poly(urethane-imide) thin films, the residual stress progressively decreased with increase in temperature and reached '0' at a particular temperature. This is because above that temperature all the molecular motions are onset leading to increased chain mobility. Because of their chain mobilities, the polymers are capable of relaxing out the stress and hence the stress component becomes zero. This temperature is taken as the T_g (glass transition temperature) of the material. During the cooling process, below the T_g of the material, the chain mobility was restricted leading to building up

of stress. It can be seen from Figure 5. The cooling path did not follow the heating cycle exactly and the slope of the cooling cycle was steep and then the stress reached higher value than the value of the heating cycle. This is due to the evaporation of the moisture in the poly(urethane-imide) thin films during the heating cycle.

TEC is a function of molecular orientation. High molecular orientation gives rise to low TEC and hence the residual stress is low. Generally in the 6FDA-based poly(urethane-imide), polymer orientation is greatly reduced leading to the high TEC, which results in high residual stress.²⁵ When compared with poly(urethane-imide) thin films, the residual stress decreased with increase in PU content. Generally polyurethane has very low T_g (about -60°C) and since the molecular motions are onset leading to relaxation and hence the residual stress component decreases. This is evident from the residual stress and the slope of the cooling curve. It can be seen that the overall T_g of the polymer network is much higher than the pure PU and this result proves the formation of crosslinked network (Table V).

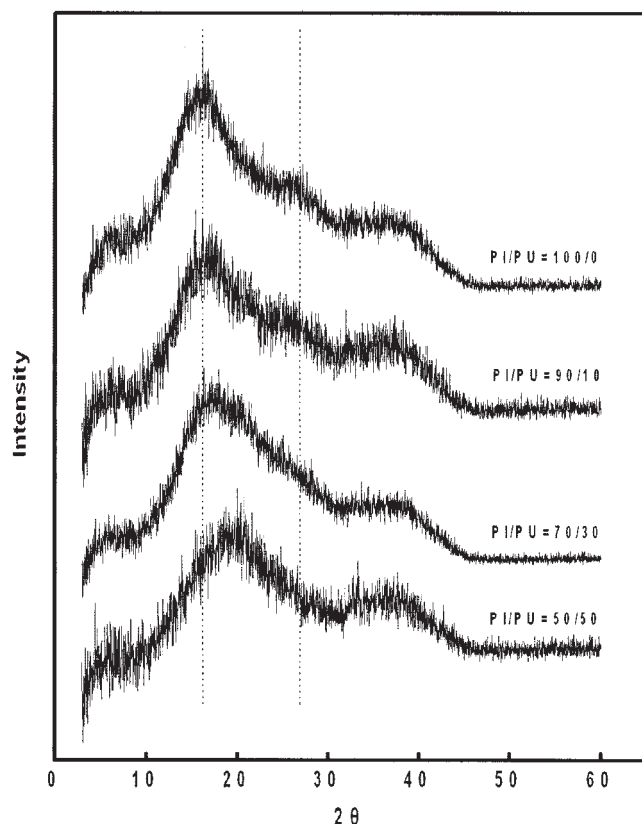


Figure 6 WAXD pattern for reflection mode of poly(urethane-imide)s.

Morphological structure

The morphological structure of the poly(urethane-imide) thin films can be obtained from WAXD patterns in Figure 6. All the poly(urethane-imide) thin films exhibited structureless amorphous halo indicating the absence of crystallinity. These observations indicate that they are irregularly packed together. The lack of regular intermolecular packing might be the result of the increased chain mobility because of low T_g . The presence of bulky linkages in the polyimide induced amorphous halo patterns. With increase in PU contents, poly(urethane-imide) thin films were expected to be amorphous. From the peak maximum of the amorphous halo, the d -spacing value was calculated (Table III). The d -spacing value was found to decrease with increase in the of PU content. This trend can be explained that the irregular polyurethane chain plays an important role in the formation of the high molecular packing order.

Thermal property

The thermal stability of the poly(urethane-imide) thin films was measured by thermogravimetric analysis (TGA). The 5 and 10% weight loss temperatures in a nitrogen atmosphere are given in Table IV and the ther-

mograms are shown in Figure 7. Thermograms were recorded in nitrogen atmosphere at a heating rate of 10°C/min. Pure polyimide exhibited single step degradation pattern and the 5 and 10% weight loss temperatures were 470.5 and 514.5°C respectively. With the incorporation of PU, the thermograms exhibited two-step degradation patterns and the pure polyurethane again gave a single step degradation pattern. The first step degradation is due to the degradation of PU backbone and the second step degradation is due to the degradation of PI.²⁶ With increase in PU content, the 5 and 10% weight loss temperatures of the poly(urethane-imide) thin films decreased as expected. Also the weight residue increased with increase in PU content. Compared to pure polyurethane, poly(urethane-imide) thin films exhibited better thermal stabilities due to the presence of the heterocyclic imide groups without the phase separation in poly(urethane-imide) which was confirmed by DSC (Fig. 7).

The chain mobility can be related to the residual stress. Table V shows elongation, TEC, and T_g of poly(urethane-imide) thin films measured by DMTA. T_g decreased with the increase of PU content as 300, 254, 248, and 239°C. It showed the introduction of flexible PU chain increased the chain mobility and T_g decreased. Elongation and TEC increased with increase in PU content as seen in Table V. It is due to the increased chain mobility with increase in PU content and it can increase the residual stress. However, the residual stress decreased with increase in PU content as seen in Table III and it shows that the residual stress of poly(urethane-imide) thin films does not only depends on the chain mobility such as elongation, TEC and glass transition temperature (T_g) but also depends on the morphological structure on poly(urethane-imide) thin films.

Mechanical property

The mechanical properties of the poly(urethane-imide) thin films were calculated from the nano-indentation behavior and load-displacement curves with the Berkovich indenter. The remarkable elastic-plastic behavior of the poly(urethane-imide) thin films with PU contents is illustrated in Figure 8 with the composition of PI/PU.

TABLE IV
Thermal Stabilities of Poly(urethane-imide)s

Poly(urethane-imide)	Thermal properties		
	Weight loss		Residue (%) at 800°C
	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	
PI/PU = 100/0	470.5	514.5	51.4
PI/PU = 90/10	321.1	375.2	49.1
PI/PU = 70/30	298.3	323.4	41.2
PI/PU = 50/50	282.9	303.2	31.5
PI/PU = 0/100	240.6	259.9	7.4

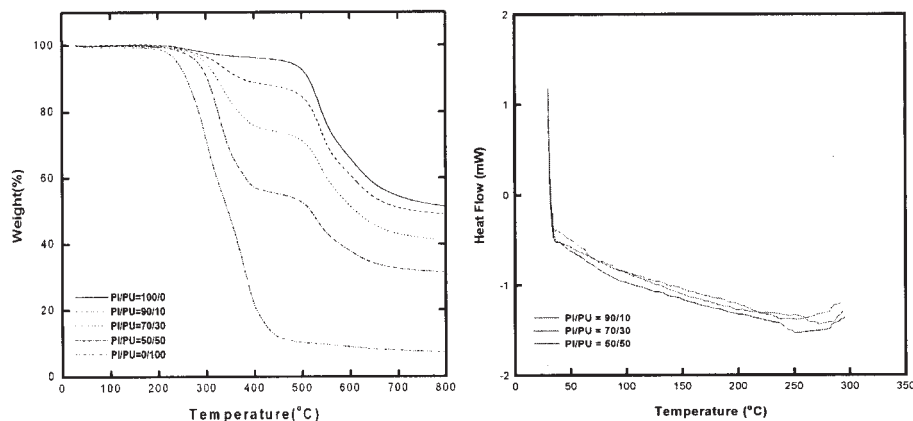


Figure 7 TGA thermograms and DSC of poly(urethane-imide)s.

Table VI summarizes the changes in the load, modulus, and hardness with a fixed penetration depth for poly(urethane-imide) thin films. With a fixed penetration depth as 1115 nm, the load and modulus increased with the introduction of PU but they gradually decreased with increase in PU contents as $8.34 > 5.24 > 3.09$ mN and $6.75 > 3.22 > 1.70$ GPa. Hardness evenly decreased with increase in PU contents as $0.344 > 0.339 > 0.236 > 0.153$ GPa. When PI/PU = 100/0 and PI/PU = 90/10 were compared, modulus slightly increased from 5.61 to 6.75 GPa. It shows that only 10% PU contents do not effect any remarkable change in modulus. Generally low intermolecular interaction and molecular packing order show low modulus and hardness. As seen in WAXD data, the intermolecular distance decreased with increase in PU contents resulting in high intermolecular interaction and molecular packing order. From WAXD data, the modulus and hardness had to increase with increase in PU contents but actually they decreased. It is because the chain mobility increased to a greater extent with increase in flexible PU contents. It shows that the modulus and hardness of poly(urethane-imide) thin films depend on the content of PU and they are not affected by only the morphology but also by the chain mobility which was observed from thermal property by DMTA.

TABLE V
Thermal Expansion Properties and Glass Transition Temperature of Poly(urethane-imide) Thin Films

Poly(urethane-imide)	Elongation ^a (%)	TEC ^b (ppm/°C)	T_g^c (°C)
PI/PU = 100/0	1.5	90.4	300
PI/PU = 90/10	1.6	95.9	254
PI/PU = 70/30	1.8	107	248
PI/PU = 50/50	1.9	108	239

^a Measured by DMTA.

^b Averaged over 50–200°C using DMTA.

^c Measured by DMTA with ramping rate at 5.0°C/min and frequency at 1 Hz.

CONCLUSIONS

Poly(urethane-imide) thin films were prepared by the reaction between MA end-capped soluble polyimide (PI) and acrylate end-capped polyurethane (PU) and the effect of PU content on the residual stress behavior, dielectric constant, thermal property, morphology, and mechanical property was studied. The completion of synthesis of poly(urethane-imide)s was confirmed by FTIR. Dielectric constant of poly(urethane-imide) thin films by optical method (474.1 THz) decreased with increase in PU contents as $2.46 > 2.45 > 2.42 > 2.39$. Also residual stress decreased with the increase in PU contents. Especially PI/PU = 50/50 showed 5 MPa residual stress and it is very low value compared with the residual stress of other electronic materials reported up to now. Poly(urethane-imide)

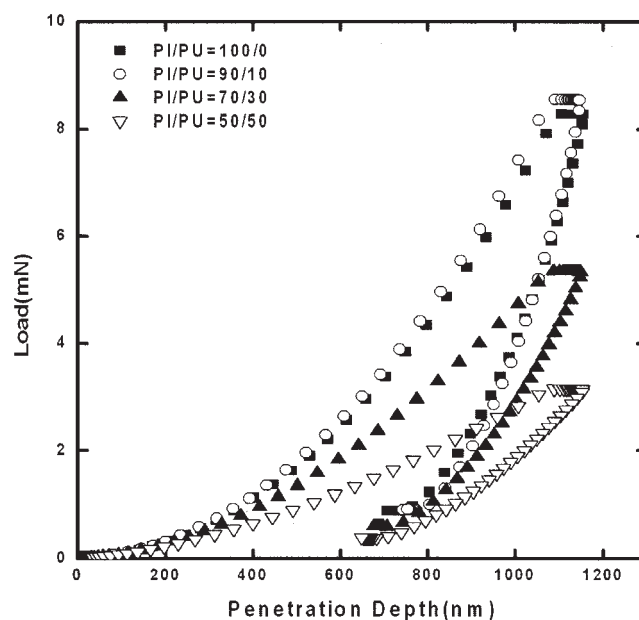


Figure 8 Nanoindentation traces for poly(urethane-imide) thin films according to the polyurethane content.

TABLE VI
Nano-Indentation Data as a Function of the
Polyurethane Content for Poly(urethane-imide) Thin
Films at a Depth of 1115 nm

Poly(urethane-imide)	Depth (nm)	Load (mN)	Modulus (GPa)	Hardness (GPa)
PI/PU = 100/0	1115	8.09	5.61	0.344
PI/PU = 90/10	1115	8.34	6.75	0.339
PI/PU = 70/30	1115	5.24	3.22	0.236
PI/PU = 50/50	1115	3.09	1.70	0.153

thin films exhibited better thermal stabilities due to the presence of the imide groups than pure polyurethane. They were stable under 250°C and it indicates that synthesized poly(urethane-imide) thin films are thermally good for the engineering applications. The elongation and TEC increased with increase in PU content and T_g decreased. The intermolecular distance by WAXD, the modulus and hardness by Nano-indentation decreased with increase in the flexible PU. Finally the residual stress of poly(urethane-imide)s were strongly affected by the morphological structure, chain mobility, and modulus.

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