

Syntheses and Properties of Urethane Prepolymers and Their Corresponding Crosslinked Films

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Synopsis

Trimethylol propane (TMP), polyglycol (PG), and toluene diisocyanate (TDI) were reacted in various molar ratios to produce TMP-TDI-PG-urethane prepolymers and then mixed with equivalent isocyanate generator (Desmodur AP-Stable) in a mixture of *m*-cresol and naphtha to give polyurethane varnishes which finally became crosslinked films by the casting method. The mechanical properties and viscoelasticities of the PG-modified and PG-free polyurethane crosslinked films and the practicability of magnet wires coated with them were studied in this article. Three different PGs used in this experiment were polyethylene glycol, PEG (# 400), polypropylene glycols, PPG (# 1000) and PPG (# 2000). In the case of adding PEG (# 400) for modification, strength at break increased but elongation did not change. Meanwhile, glass transition temperature (T_g) shifted to lower temperature with increasing molar ratio. In the case of adding PPG (# 1000) and PPG (# 2000) for modification, the samples changed their mechanical properties from hard and brittle to soft and tough. With increasing molar ratios, strength at break initially increased and then decreased gradually, and elongation varied a lot and was consistently contrary to strength at break. T_g occurred at two regions: one at high temperature above 100°C for small molar ratios and the other at low temperature below 100°C for high molar ratios. Besides, for all PG-modified polyurethane crosslinked films, strength at break showed a local maximum at TMP/TDI/PG = 1/1/0.5, which indicated their homogeneous structures. The molar ratios of PG-modified urethane prepolymers, which are suitable for manufacturing practical magnet wires according to testing method JIS-C-3211, are as follows: TMP/TDI/PPG (# 1000) = 1/1/0.15–0.35 and TMP/TDI/PPG (# 2000) = 1/1/0.10. PEG (# 400)-modified magnet wires were not accepted on the aging test. The properties of crosslinked films of practical magnet wires are generally as follows: strength at break at 200–700 kg/cm², elongation less than 41%, and T_g at 100–200°C.

INTRODUCTION

Polyurethane resins, with their outstanding characteristics, are widely used in many industrial fields such as coatings, elastomers, foams, leathers, and fiber-treating agents. The purpose of this research is to study the mechanical properties of thermal-crosslinked polyurethane films for magnet wires. Polyurethane varnishes are generally synthesized as follows^{1–6}: isocyanates or blocked isocyanates are reacted with various polyols to give hydroxy-terminated prepolymers and then mixed with crosslinking agents to form coating varnishes which are used for the manufacture of magnet wires. Some modified polyurethane varnishes^{7–11} for improvement in certain properties are also reported. Takizawa et al.¹² synthesized polyurethane varnish with TMP, TDI, and Desmodur AP-Stable forming brittle crosslinked film. Okada et al.¹³ reported a polyesterurethane insulating varnish. They synthesized hydroxy-terminated polyester with dimethyl terephthalate, ethylene glycol, and glycerol. Then the polyester was reacted with TDI mixed with Coronate AP-Stable for producing

coating varnish, which was used to produce high-quality magnet wire. Synthesis of PG-modified polyurethane varnishes in this work is as follows: TMP, TDI, and PG were reacted with various molar ratios to form hydroxy-terminated urethane prepolymers of different molecular weights and then the prepolymers were mixed with equivalent Desmodur AP-Stable in a mixture of *m*-cresol and naphtha to give the desired varnishes. The purpose of introducing different kinds of PGs and changing their molar ratios is to improve the mechanical properties of the corresponding crosslinked films and the mechanical properties of those films were measured and studied by the Instron Universal Tester and the Rheovibron DDV-II Dynamic Viscoelastomer.

EXPERIMENTAL

Materials

Monomers and Polyglycols

Monomers used in synthesizing urethane prepolymers and Desmodur AP-Stable were reagent-pure TMP purchased from BDH Chemicals, Ltd., England, and TDI and phenol, which were technical grades and commercially available. Polyglycols used in synthesizing urethane prepolymers were polyethylene glycol with $M_n = 400$ [PEG(#400)], which was technical pure and commercially available, polypropylene glycol with $M_n = 1000$ [PPG(#1000)], purchased from Hayashi Chemical, Ltd., Japan, and polypropylene glycol with $M_n = 2000$ [PPG(#2000)], supplied by Wako Chemical, Ltd., Japan. Both of the polypropylene glycols were reagent grades.

Solvents

Three organic solvents were used in experiment. Anisole and *m*-cresol were reagent grades and purchased from Wako Chemical Ltd. Naphtha was technical grade and supplied by China Petrochemical Company.

Copper Wire

Copper wire used in processing was annealed and pretreated, with a diameter of 0.6 mm and supplied by Tatung Cable Company.

Instruments

Some instruments used in this work included the Instron Universal Tester, the Rheovibron DDV-II Dynamic Viscoelastometer, a pinhole tester, a baking oven, gel permeation chromatography, and a rotary viscometer.

Synthesis

Urethane Prepolymers

TMP-TDI-PG-Urethane Prepolymers. Into a flask equipped with stirrer, reflux condenser, and inert gas blanket were charged calculated quantities of

TDI, PG, and anisole under a nitrogen atmosphere. The mixture was gradually heated to 80–85°C for 30 min and then cooled to room temperature. Into the mixture, a calculated quantity of TMP was added, the temperature was raised to 50°C for 1 h and at 110–120°C for another 1 h for completion. The resultant mixture was hydroxy-terminated urethane prepolymers.

TMP-TDI-Urethane Prepolymers. Into a flask equipped as above were charged calculated quantities of TMP and anisole under a nitrogen atmosphere. The mixture was heated to about 67°C until TMP was melted. Into the mixture a calculated quantity of TDI was added so slowly that large exotherm was avoided. After adding TDI, the mixture was heated to 100°C for 2 h and at 120°C for another 2 h to produce hydroxy-terminated urethane prepolymers.

Crosslinking Agent (Desmodur AP-Stable)

Into a flask equipped as above were charged calculated quantities of TMP and phenol. The mixture was heated to about 50°C for dissolution and then cooled to room temperature. Into the mixture a calculated quantity of TDI was added, and the temperature was slowly raised to 110°C for 1 h and to 140°C for completion. The product, being brittle at room temperature, is hereinafter referred to as Desmodur AP-Stable.

Processing

Film Casting

A processing solution of solid content $35 \pm 10\%$, viscosity 10 ± 2 P was prepared by dissolving and mixing hydroxy-terminated urethane prepolymer and equivalent Desmodur AP-Stable in a mixture of *m*-cresol and naphtha. A little portion of such solution was poured on a smooth surface of aluminum foil and flowed into a thin circle of diameter 10 cm. Upon baking at 200°C for 20 min, a cross-linked film tightly adhered to aluminum foil was formed. After being put into a hydrochloric acid solution (1/1) to dissolve aluminum foil, a smooth crosslinked polyurethane film of thickness within 1 mm is available.

Wire Coating

Into a test tube, about 15 cm long, were charged the above solution as in film casting. The tube was covered with a steel plate having a small round hole in the center as a die. A segment of annealed, rustless, degreased copper wire of 0.6 mm in diameter and 20 cm long was inserted into the tube through the die and drawn back to be baked at 200°C for 15 min in an oven, where solvents were volatilized and resins were crosslinked. Replaced dies and repeated the same procedure four times to give polyurethane magnet wire of overall diameter within 0.672 mm.

Testing Method

Stress-Strain Test

The crosslinked polyurethane film was cut into a dumbbell shape of length 4 cm, breadth at neck within 1 cm, and thickness less than 0.5 mm. An Instron

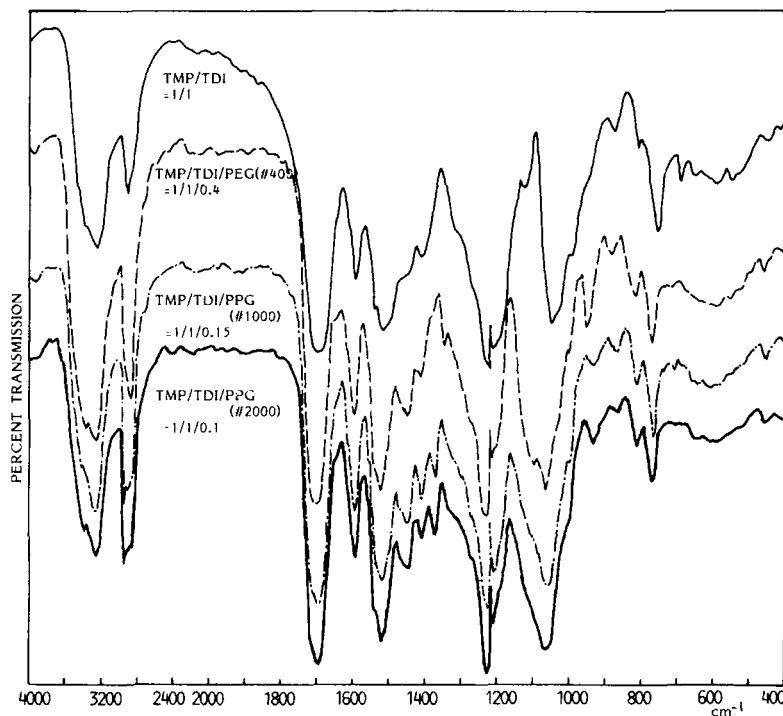


Fig. 1. Infrared spectra of synthetic TMP-TDI-urethane prepolymer and TMP-TDI-PG-urethane prepolymers in KBr pellet.

Universal Tester with a load cell of 500 g was used to study the stress-strain behavior of the samples at room temperature at a drawing speed of 8 cm/min.

Dynamic Viscoelasticity Test

The sample was shaped into a rectangle of length 2–3 cm, breadth 0.5 cm, and thickness less than 0.5 mm. A Rheovibron DDV-II Dynamic Viscoelastometer was used to study the dynamic mechanical behavior of the films in the temperature range of 25–220°C, at a frequency of 110 Hz. The loss tangent ($\tan \delta$) is directly measured and the calculation of complex modulus (G^*), storage modulus (G'), and loss modulus (G'') is outlined below, respectively:

$$G^* = \frac{2}{A \cdot D - K} \cdot \frac{L}{S} \times 10^9 \text{ dyn/cm}^2$$

$$G' = |G^*| \cos \delta \text{ dyn/cm}^2$$

$$G'' = |G^*| \sin \delta = G' \tan \delta \text{ dyn/cm}^2$$

where A = amplitude factor, D = dynamic force, K = error constant at zero length, L = length of sample, S = cross-sectional area of sample.

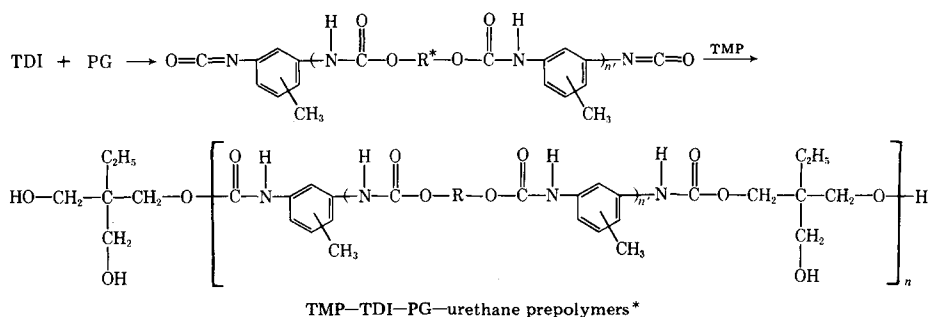
Magnet Wire Test

The manufactured magnet wires was all tested according to Testing Method JIS-C-3211.

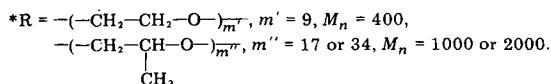
RESULTS AND DISCUSSION

Preparation of Urethane Prepolymers

TDI was reacted with PG to give isocyanate-terminated polyurethane, and then TMP was added to produce TMP-TDI-PG-urethane prepolymer as shown in Formula 1, where R represents polyglycol segments. Changing the molar ratio of TMP/TDI/PG and using different PGs gave urethane prepolymers of various molecular weight distribution (MWD). Without adding any PG in Formula 1, TDI was reacted with TMP directly to produce TMP-TDI-urethane prepolymer of $n' = 0$. Changing the molar ratio of TMP/TDI also gave urethane prepolymer of different MWD. Furthermore, the product synthesized from $\text{TMP/TDI} < 1$ was crosslinked and insoluble, but that of $\text{TMP/TDI} > 2$ was a mixture of $n = 1$ oligomer and TMP itself.



Formula 1

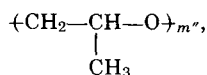


Crosslinking Reaction of Urethane Prepolymers

Urethane prepolymers were mixed with equivalent Desmodur AP-Stable in a mixture of *m*-cresol and naphtha to form coating solutions and then casted on a substrate or coated on copper wire to be baked at 200°C in an oven for 15–20 min to give crosslinked network structures. In this crosslinking reaction, excess Desmodur AP-Stable results in formation of allophanate linkage, but insufficient Desmodur AP-Stable produces hydroxy-remaining structure. When TMP-TDI-PG-urethane prepolymers were used, polyglycol segment R included



$m' = 9$, and



$m'' = 17 \text{ or } 34$.

By the way, $n' = 0$ represented the case PG-free TMP-TDI-urethane prepolymers were used. The properties of crosslinked polyurethanes depend on the existence and structure of R and the value of n' : large n' or R results in low crosslinking density but small n' gives hard and brittle crosslinked films.

* Molar ratio of TMP-TDI-PG-urethane prepolymers: $\text{TMP/TDI/PG} = 1/1/0.05\text{--}1.0$, and molar ratio of TMP-TDI-urethane prepolymers ($n' = 0$): $\text{TMP/TDI} = 0.5\text{--}2.5/1$.

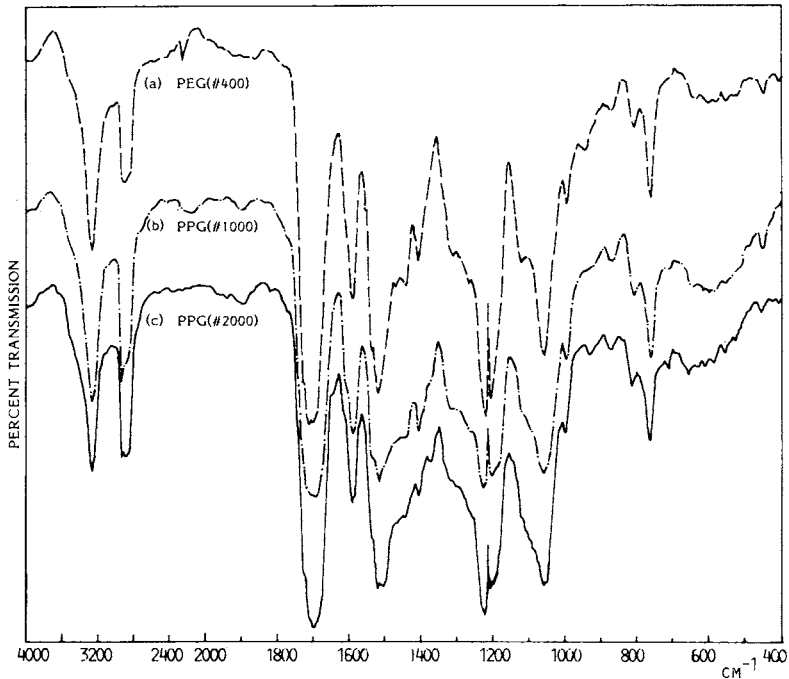


Fig. 2. Infrared spectra of the crosslinked films prepared from TMP-TDI-PG-urethane prepolymers and Desmodur AP-Stable: (a) TMP/TDI/PEG(#400) = 1/1/0.4; (b) TMP/TDI/PPG(#1000) = 1/1/0.15; (c) TMP/TDI/PPG(#2000) = 1/1/0.1.

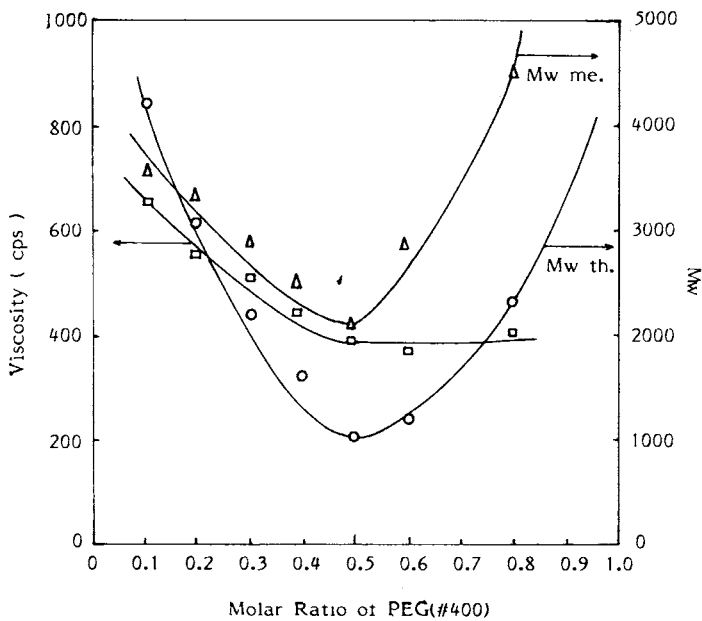


Fig. 3. PEG(#400) molar ratio dependence of viscosity of coating solutions based on TMP-TDI-PEG(#400)-urethane prepolymers at 36% solid content. $M_w th. = \frac{\sum N_i M_i^2}{\sum N_i M_i}$, $M_i = 134 + n_i [174 + n_i'(400 + 174) + 134]$ according to formula 1 and $N_i =$ mole fraction.

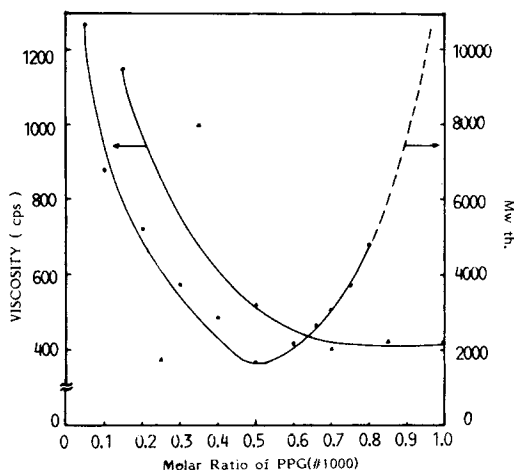


Fig. 4. PPG(#1000) molar ratio dependence of viscosity of coating solutions based on TMP-TDI-PPG(#1000)-urethane prepolymers at 36% solid content. $M_w \text{ th.} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$, $M_i = 134 + n_i[174 + n_i'(1000 + 174) + 134]$ according to formula 1 and $N_i =$ mole fraction.

IR Spectra of Synthetic Urethane Prepolymers and Their Corresponding Crosslinked Films

The IR spectra of one TMP-TDI-urethane prepolymer and three TMP-TDI-PG-urethane prepolymers are shown in Figure 1. It can be seen that the characteristic absorption peaks of many functional groups in these samples occurred as follows: hydroxy group at 3400 cm^{-1} , urethane —NH— stretching at 3300 cm^{-1} , bending at 1520 cm^{-1} , methylene or alkyl groups at 2900 cm^{-1} , carbonyl group at 1700 cm^{-1} , and benzene ring at 1600 and 1500 cm^{-1} . Furthermore, the IR spectra of PPG-containing urethane prepolymers show an absorption peak at 1370 cm^{-1} owing to a greater fraction of methyl group, and such a peak disappeared in the case of PEG-containing urethane prepolymers. The IR spectra of crosslinked films corresponding to TMP-TDI-PG-urethane prepolymers are shown in Figure 2. These spectra show no more absorption peak at 3400 cm^{-1} because of losing the hydroxy group through crosslinking reaction. Moreover, the spectra of PPG(#1000)- and PPG(#2000)-containing crosslinked films show a stronger absorption peak at 2900 cm^{-1} than that of PEG(#400)-containing crosslinked film because the fraction of methyl group is greater in the former than in the latter. Besides, the IR absorption spectra of these crosslinked films are quite analogous to one another except the absorption peak at 2900 cm^{-1} .

Influence of MWD of Urethane Prepolymers on Viscosity of Coating Solutions

MWD of TMP-TDI-PG-urethane prepolymers and viscosity of the corresponding coating solutions measured at the same conditions are shown in Figures 3, 4, and 5 representing the cases of adding PEG(#400), PPG(#1000), and PPG(#2000), respectively. It can be seen from these figures that by increasing the molar ratio of PG, the theoretical M_w decreased with a minimum at

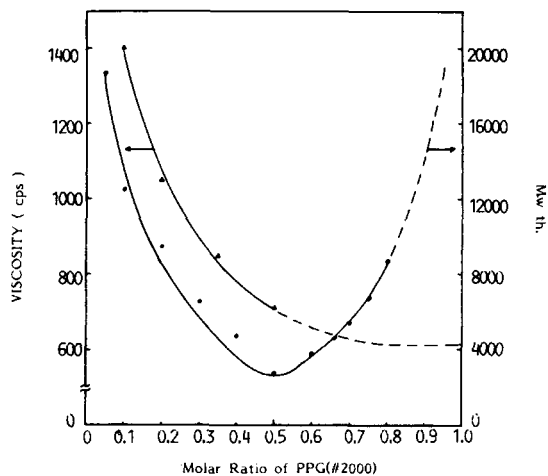


Fig. 5. PPG (#2000) molar ratio dependence of viscosity of coating solutions based on TMP-TDI-PPG (#2000)-urethane prepolymers at 33% solid content. $M_w \text{ th.} = \sum N_i M_i^2 / \sum N_i M_i$, $M_i = 134 + n_i [174 + n_i' (2000 + 174) + 134]$ according to formula 1 and $N_i = \text{mole fraction}$.

TMP/TDI/PG = 1/1/0.5 and then increased. Viscosities of coating solutions varied consistently with theoretical M_w in the range of TMP/TDI/PG = 1/1/0.05–0.5. In preparing the coating solutions, Desmodur AP-Stable, a crosslinking agent with three reactive isocyanate groups at elevated temperature, was added equivalent to the remaining hydroxy groups of urethane prepolymers. Therefore, when above TMP/TDI/PG = 1/1/0.5, more Desmodur AP-Stable was added as PG increased so that viscosities of coating solutions remained almost constant rather than increasing since the molecular weight of Desmodur AP-Stable is

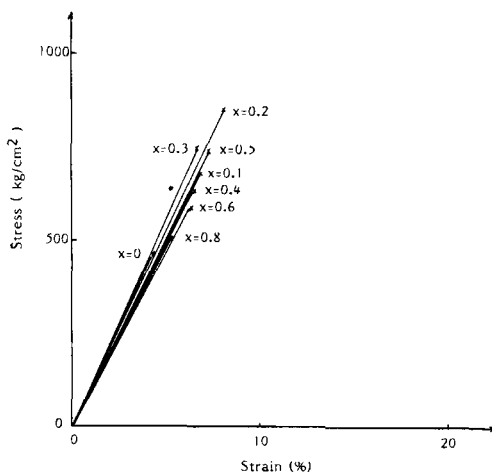


Fig. 6. Stress-strain curves of the crosslinked films prepared from TMP-TDI-urethane prepolymers and TMP-TDI-PEG (#400)-urethane prepolymers. The numerical values on the figure represent the molar ratio x of PEG (#400) in TMP/TDI/PEG (#400) = 1/1/ x except that $x = 0$ represents TMP/TDI = 1.6/1.

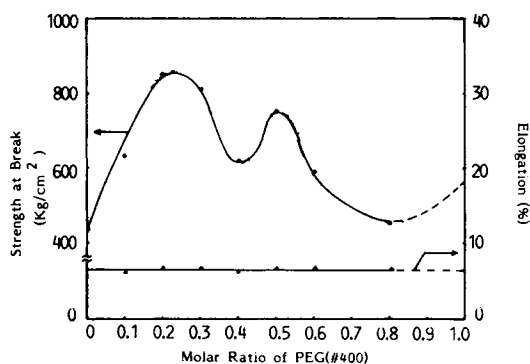


Fig. 7. PEG (# 400) molar ratio dependence of strength at break and elongation for the crosslinked films in the range of TMP/TDI/PEG (# 400) = 1/1/0–0.8.

much lower than the urethane prepolymers. Besides, the measured M_w by GPC was consistent with the theoretical M_w as shown in Figure 3.

Influence of the Composition of Urethane Prepolymers on the Stress–Strain Property of the Corresponding Crosslinked Films

The stress–strain curves of the crosslinked films prepared from different molar ratio TMP–TDI–urethane prepolymers and TMP–TDI–PEG (# 400)–urethane prepolymers are shown in Figure 6. These curves are linear and almost overlapping, indicating that these crosslinked films are strong and tough in the range of TMP/TDI = 1–2/1 and TMP/TDI/PEG (# 400) = 1/1/0–0.8. The results of strength at break and elongation for crosslinked films in the same range are shown in Figure 7. For samples in the range of TMP/TDI/PG (# 400) = 1/1/0–0.8, all strengths at break are between 857 and 434 kg/cm², and those with PEG (# 400) are higher than without PEG (# 400). With increasing molar ratio of PEG (# 400), strength at break shows a maximum at about TMP/TDI/

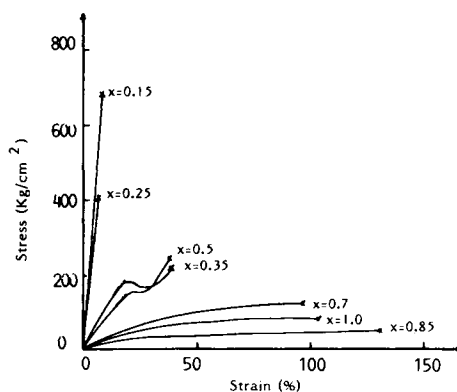


Fig. 8. Stress–strain curves of the crosslinked films prepared from TMP–TDI–PPG (# 1000)–urethane prepolymers. The numerical values on the figure represent the molar ratio x of PPG (# 1000) in TMP/TDI/PPG (# 1000) = 1/1/ x .

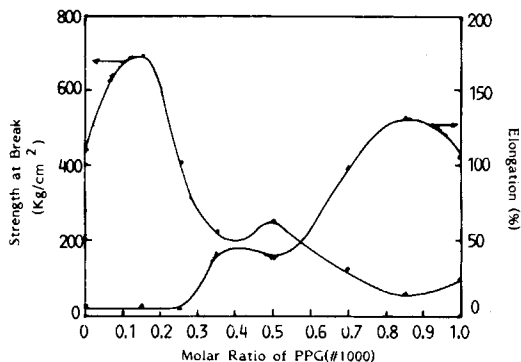


Fig. 9. PPG (# 1000) molar ratio dependence of strength at break and elongation for the crosslinked films in the range of TMP/TDI/PPG (# 1000) = 1/1/0–1.

PEG (# 400) = 1/1/0.2 and then decreases gradually except at TMP/TDI/PEG (# 400) = 1/1/0.5, where it displays a local maximum; this is probably attributed to its more homogeneous crosslinked structure which is due to the locally smaller polydispersity at this molar ratio. Elongations of the same samples are all less than 10% and the difference in molar ratio of these urethane prepolymers contributes nothing to the variation in elongation.

The stress–strain curves of crosslinked films prepared from different molar ratio TMP–TDI–PPG (# 1000)–urethane prepolymers are shown in Figure 8. Compared with those curves containing PEG (# 400) in Figure 6, these curves change roughly with molar ratios of TMP–TDI–PPG (# 1000)–urethane prepolymers. By increasing the molar ratio of PPG (# 1000) in the range of TMP–TDI–PPG (# 1000) = 1/1/0–1.0, the variation trend of the property of crosslinked films is as follows: hard and brittle, hard and strong, hard and tough, and finally soft and tough. Figure 9 shows the results of strength at break and elongation for samples in the range of the same molar ratios. Strengths at break of crosslinked films differ a lot with the increase of molar ratio of PPG (# 1000)

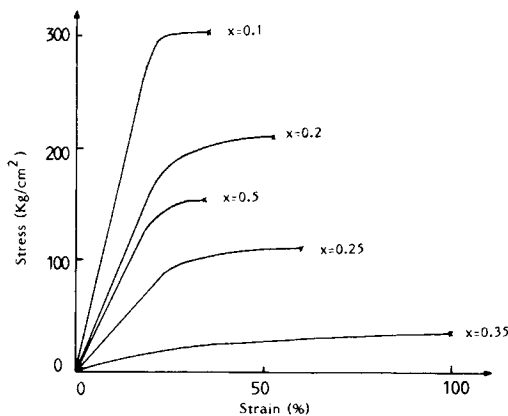


Fig. 10. Stress–strain curves of the crosslinked films prepared from TMP–TDI–PPG (# 2000)–urethane prepolymers. The numerical values on the figure represent the molar ratio x of PPG (# 2000) in TMP/TDI/PPG (# 2000) = 1/1/ x .

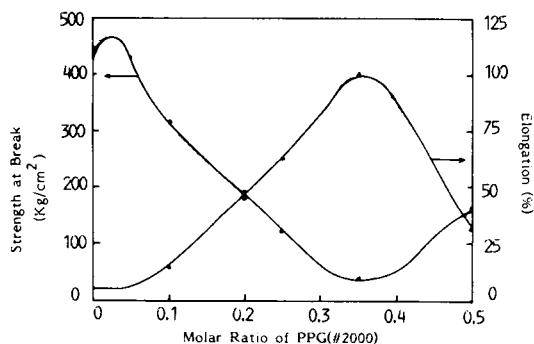


Fig. 11. PPG(#2000) molar ratio dependence of strength at break and elongation for the cross-linked films in the range of TMP/TDI/PPG(#2000) = 1/1/0–0.5.

in the range of TMP/TDI/PPG(#1000) = 1/1/0–1.0 and the maximum appears at TMP/TDI/PPG(#1000) = 1/1/0.1–0.2. Over the maximum value, they drop sharply with increasing the molar ratio of PPG(#1000) except at TMP/TDI/PPG(#1000) = 1/1/0.5, where strength at break appears a local maximum again, which occurred in the case of adding PEG(#400). Generally, strength at break relates to elongation so far as the same film being concerned. High strength at break makes low elongation, and, on the contrary, low strength at break makes high elongation. Elongations of the films prepared from TMP–TDI–PPG(#1000)–urethane prepolymers are less than 10% within TMP/TDI/PPG(#1000) = 1/1/0.25. When molar ratio becomes greater than TMP/TDI/PPG(#1000) = 1/1/0.25, they rise with the increase of molar ratio of PPG(#1000) except at TMP/TDI/PPG(#1000) = 1/1/0.5 and 1/1/1, where elongation shows a local minimum that is consistent with in the case of strength at break.

The stress–strain curves of crosslinked films prepared from different molar ratio TMP–TDI–PPG(#2000)–urethane prepolymers are shown in Figure 10. Compared with those containing PEG(#400) and PPG(#1000) in Figures 6 and 8, respectively, these curves change more roughly with molar ratios of TMP/TDI/PPG(#2000)–urethane prepolymers. The variation trend of the property of films, in the range of TMP/TDI/PPG(#2000) = 1/1/0–0.5, is as follows; hard and strong, hard and tough, and then soft and tough. Figure 11 shows the results of strength at break and elongation for the crosslinked films in the range of molar ratios of TMP/TDI/PPG(#2000) = 1/1/0–0.5. The variation trend of strength at break and elongation hereinafter is similar to that of in the case of adding PPG(#1000). By increasing molar ratios of PPG(#2000) in the range of TMP/TDI/PPG(#2000) = 1/1/0–0.5, strengths at break decrease rapidly, and elongations increase gradually except at TMP/TDI/PPG(#2000) = 1/1/0.5, where strength at break shows a local increase and elongation shows a local decrease due to its homogeneous crosslinked structure.

Influence of Composition of Urethane Prepolymers on the Viscoelasticity of the Corresponding Crosslinked Films

Experimental results on the crosslinked films prepared from different kinds of urethane prepolymers measured by Rheovibron DDV-II Dynamic Viscoe-

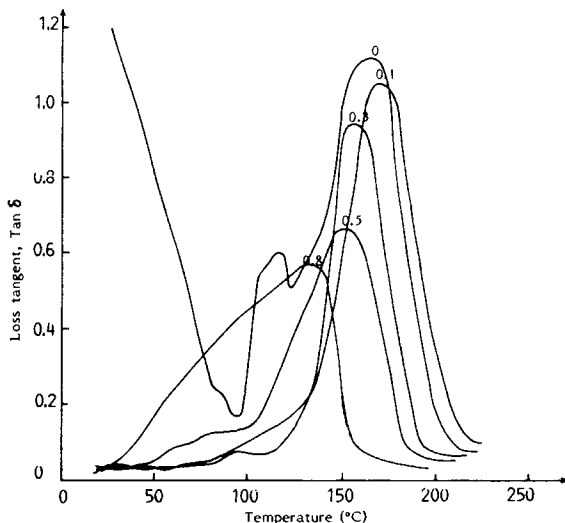


Fig. 12. Temperature dependence of loss tangent ($\tan \delta$) for PEG (#400)-containing crosslinked films. The numerical values on the figure represent the molar ratio x of PEG (#400) in TMP/TDI/PEG (#400) = $1/1/x$, except that $x = 0$ represents TMP/TDI = 1.6/1.

lastometer are displayed and discussed. The loss tangent of PEG (#400)-containing crosslinked films is shown as a function of temperature in Figure 12. The $\tan \delta$ curves show only one peak in the range from room temperature to 220°C ; the peak positions move to lower temperature with adding PEG (#400) than without it. As molar ratio of PEG (#400) in TMP-TDI-PEG (#400)-urethane prepolymers increases, the peak position shifts more to lower temperature and the $\tan \delta$ curve itself comes down. This reveals that the property of these crosslinked films has a close relationship with the existence of PEG (#400). The introduction of some PEG (#400) will result in a lower phase transition temperature, low viscosity, and high elasticity. These effects are more pronounced if more PEG (#400) is added. The storage modulus for PEG (#400)-containing crosslinked films is plotted semilogarithmically as a function of temperature,

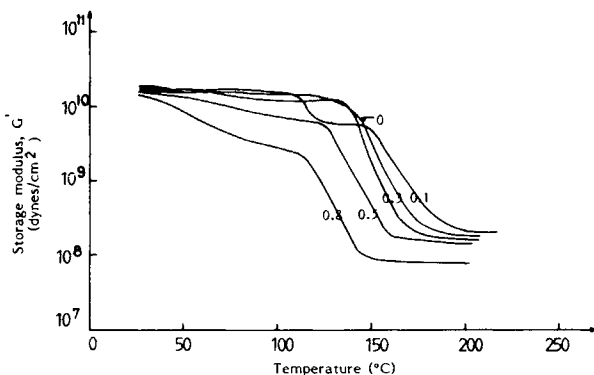


Fig. 13. Temperature dependence of storage modulus (G') for PEG (#400)-containing crosslinked films. The numerical values on the figure represent the molar ratio x of PEG (#400) in TMP/TDI/PEG (#400) = $1/1/x$, except that $x = 0$ represents TMP/TDI = 1.6/1.

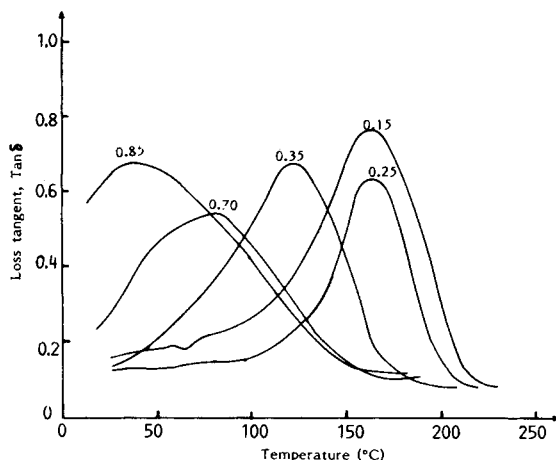


Fig. 14. Temperature dependence of loss tangent ($\tan \delta$) for PPG (#1000)-containing crosslinked films in the range of TMP/TDI/PPG (#1000) = 1/1/0–1.0. The numerical values on the figure represent the molar ratio of PPG (#1000).

as shown in Figure 13. Starting from room temperature, storage modulus remains almost unchanged until about 100°C and therefore decreases as temperature continuously rises. This phenomenon occurs only for those films in the range of TMP/TDI/PEG (#400) = 1/1/0.1–0.5. For those films containing more PEG (#400), storage modulus decreases gradually as soon as the temperature rises originally.

In the case of adding PPG (#1000) as polyglycol, the phase transition temperature of crosslinked films can be divided into two regions on the basis of molar ratio of PPG (#1000) in the urethane prepolymers. The loss tangent of PPG (#1000)-containing crosslinked films is shown as a function of temperature in Figure 14. Within the range of TMP/TDI/PPG (#1000) = 1/1/0–0.5, hard

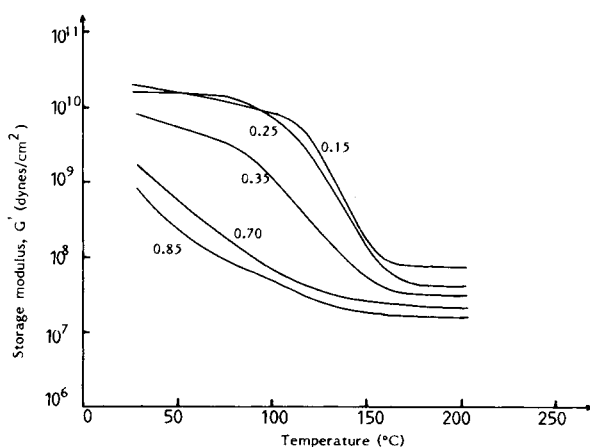


Fig. 15. Temperature dependence of storage modulus (G') for PPG (#1000)-containing crosslinked films. The numerical values on the figure represent the molar ratio x of PPG (#1000) in TMP/TDI/PPG (#1000) = 1/1/ x .

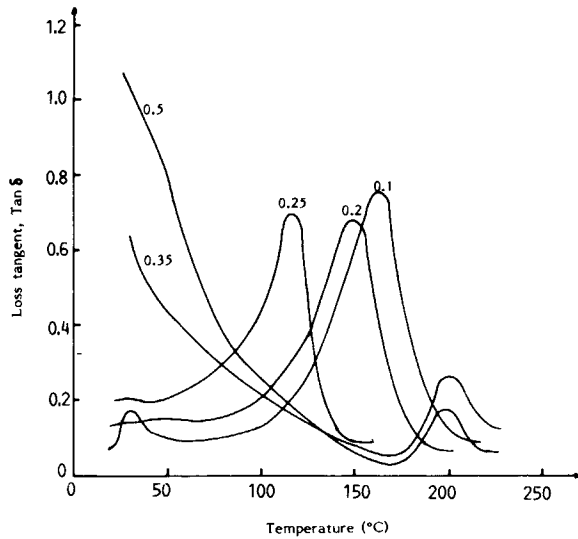


Fig. 16. Temperature dependence of loss tangent ($\tan \delta$) for PPG(#2000)-containing crosslinked films in the range of TMP/TDI/PPG(#2000) = 1/1/0–0.5. The numerical values on the figure represent the molar ratio of PPG(#2000).

segments dominate in films, and this contributes their maximum $\tan \delta$ peaks appearing between 100°C and 200°C. When above TMP/TDI/PPG(#1000) = 1/1/0.5, soft segments dominate in films and their maximum $\tan \delta$ peaks occur in the range from 0°C to 100°C. Furthermore, the maximum peak shifts to lower temperature as the molar ratio of PPG(#1000) increases in both regions. The storage modulus for PPG(#1000)-containing crosslinked films is plotted semilogarithmically as a function of temperature in Figure 15. It can be seen that storage modulus–temperature curves shift down with increasing molar ratio of PPG(#1000), and this phenomenon means that the addition of PPG(#1000) results in soft crosslinked films and lowers their phase transition temperatures.

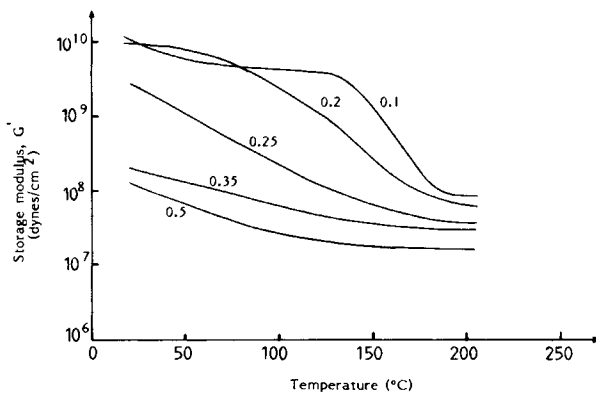


Fig. 17. Temperature dependence of storage modulus (G') for PPG(#2000)-containing crosslinked films. The numerical values on the figure represent the molar ratio x of PPG(#2000) in TMP/TDI/PPG(#2000) = 1/1/ x .

TABLE I
 Test Results of PG-Containing Polyurethane Magnet Wires^a

PG Molar ratio TMP/TDI/PG	Appear- ance	Pin- hole test	Flexi- bility	Aging test	Heat shock test	Acid resist.	Alkali resist.	Oil resist.	Sol- vent resist.	Re- marks
PEG (# 400)										
1/1/0.1	X	O	X	X	X	X	O	O	O	
1/1/0.2	X	O	O	X	O	O	O	O	O	
1/1/0.3	X	O	X	O	O	O	O	O	O	
1/1/0.4	X	O	O	X	O	O	O	O	O	
1/1/0.5	X	O	O	X	O	O	O	O	O	
1/1/0.6	X	O	O	X	O	O	O	O	O	
1/1/0.8	X	O	O	X	O	O	O	O	O	
PPG (# 1000)										
1/1/0.05	—	—	—	—	—	—	—	—	—	b
1/1/0.10	—	—	—	—	—	—	—	—	—	b
1/1/0.15	O	O	O	O	O	O	O	O	O	
1/1/0.20	O	O	O	O	O	O	O	O	O	
1/1/0.25	O	O	O	O	O	O	O	O	O	
1/1/0.35	O	O	O	O	O	O	O	O	O	
1/1/0.50	X	—	—	—	—	—	—	—	—	c
1/1/0.70	X	—	—	—	—	—	—	—	—	c
1/1/0.85	X	—	—	—	—	—	—	—	—	c
1/1/1.00	X	—	—	—	—	—	—	—	—	c
PPG (# 2000)										
1/1/0.10	O	O	O	O	O	O	O	O	O	
1/1/0.20	X	O	X	O	O	O	O	O	O	c
1/1/0.25	X	O	X	X	O	O	O	O	O	c
1/1/0.35	X	X	X	X	X	X	X	X	X	c
1/1/0.50	X	X	X	X	X	X	X	X	X	c

^a O: accepted; X: rejected; —: unmeasured.

^b The urethane prepolymer was insoluble in solvents.

^c The manufactured magnet wires adhered together to ambient temperature.

The trend of viscoelasticity variation of PPG (# 2000)-containing crosslinked films is quite similar to that of PPG (# 1000)-containing films. The difference is that the fraction of the soft segment is greater in the former than in the latter at the same molar ratio. Therefore, the maximum phase transition temperature occurs at 100–200°C for films in the range of TMP/TDI/PPG (# 2000) = 1/1/0–0.25 and below room temperature for those films above TMP/TDI/PPG (# 2000) = 1/1/0.35, respectively, as shown in Figure 16. Also, Figure 17 shows temperature dependence of the storage modulus semilogarithmically for crosslinked films in the range of TMP/TDI/PPG (# 2000) = 1/1/0–0.5. Within the range of TMP/TDI/PPG (# 2000) = 1/1/0–0.25, the hard segment dominates in the composition of films, and this also contributes maximum $\tan \delta$ peaks occurring at the high temperature region. Meanwhile, the storage modulus drops down quickly after about 100°C, and the storage modulus–temperature curves also shift down with the increasing molar ratio of PPG (# 2000). But, above TMP/TDI/PPG (# 2000) = 1/1/0.35, the soft segment dominates in composition of crosslinked films, and, therefore, maximum $\tan \delta$ peaks appear below room temperature and the storage modulus decreases smoothly as a function of temperature.

Test Results of Magnet Wires

PG-modified polyurethane magnet wires with a naked diameter of 0.6 mm were manufactured and tested. Test results of these magnet wires are listed in Table I. All PEG(#400)-modified polyurethane magnet wires manufactured from coating varnishes within the molar ratio of TMP/TDI/PEG(#400) = 1/1/0.1–0.8 are tested unsatisfactory, especially for the aging test. PPG(#1000)-containing urethane prepolymers in the range of TMP/TDI/PPG(#1000) = 1/1/0–0.1 are insoluble in a mixture of *m*-cresol and naphtha because of their higher molecular weights so that they cannot be processed for manufacturing magnet wires. Urethane prepolymers within the molar ratio of TMP/TDI/PPG(#1000) = 1/1/0.15–0.35, with moderate molecular weights or proper viscosity of coating solutions, are easily processed to manufacture magnet wires and tested acceptable for mass production. When above TMP/TDI/PPG(#1000) = 1/1/0.5, the fraction of polyglycol increases and the crosslinking density decreases in crosslinked films so that magnet wires manufactured in this range are also rejected because they adhere together at room temperature. In the case of adding PPG(#2000) as polyglycol, magnet wires manufactured are acceptable only at a molar ratio of TMP/TDI/PPG(#2000) = 1/1/0.1. Larger than TMP/TDI/PPG(#2000) = 1/1/0.2, magnet wires are no longer accepted because they adhere together at room temperature.

Relationship between Film Property of Magnet Wires and Their Corresponding Stress–Strain Behavior and Viscoelasticity

The purpose of introducing polyglycols is to improve the flexibility of the magnet wires that would be otherwise very brittle. PEG(#400)-modified polyurethane magnet wires will not pass both flexibility and aging tests no matter what molar ratios would be in the range of TMP/TDI/PEG(#400) = 1/1/0.1–0.8. In the case of adding PPG(#1000) and PPG(#2000) for modification, a small fraction of PG in the urethane prepolymers will improve flexibility and pass all tests; but the addition of more PG will degrade the flexibility and chemical resistances because of great fraction of PG chain and low crosslinking density. Table II shows the stress–strain properties of crosslinked films, which correspond to some practical polyurethane magnet wires, and all samples possess strength at break higher than 200 kg/cm² and elongation less than 50%. Furthermore, the structure of the crosslinked films of practical polyurethane magnet wires is

TABLE II
Stress–Strain Properties of PG-Containing Polyurethane Crosslinked Films Corresponding to Practical Magnet Wires

Polyglycol (PG)	Molar ratio TMP/TDI/PG	Strength at break (kg/cm ²)	Elongation (%)	Remarks
PPG(#1000)	1/1/0.15	686	<10	
PPG(#1000)	1/1/0.25	404	<10	
PPG(#1000)	1/1/0.35	219	41	
PPG(#2000)	1/1/0.10	303	35	
—	—	492	<10	commercial product

mainly composed of hard segments and the maximum $\tan \delta$ peak occurs at a high temperature region from 100°C to 200°C.

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References

1. M. Hayashizaki and M. Nakano, polyurethane electrically insulating coatings, Jpn. Kokai 74, 113,832 (1974); *Chem. Abstr.*, **83**, 99387e (1975).
2. M. Fukuchi, urethane polymer electrically insulating coating materials, Jpn. Kokai 79, 45,343 (1979); *Chem. Abstr.*, **91**, 92663y (1979).
3. M. Hayashizaki and M. Nakano, polyurethane insulating varnishes, Jpn. Kokai 77, 00,941 (1977); *Chem. Abstr.*, **86**, 157151y (1977).
4. K. Matsushita, Y. Suzuki, and K. Fujisaki, insulating varnish compositions, Jpn. Kokai 76, 135,933 (1976); *Chem. Abstr.*, **86**, 108097b (1977).
5. M. Kawaguchi, H. Nakabayashi, and M. Miyake, polyurethane insulating varnishes, Jpn. Kokai 75, 135,126 (1975); *Chem. Abstr.*, **84**, 75815n (1976).
6. T. Kiriya, T. Yamada, Y. Tabe, K. Aihara, and T. Fukuda, heat-resistant electric insulators, Jpn. Kokai 78, 123,437 (1978); *Chem. Abstr.*, **90**, 88459y (1979).
7. J. Lewalter, R. Merten, W. Zecher, and W. Duenwald, heterocyclic polyisocyanates, Ger. Offen. 2,750,772 (1979); *Chem. Abstr.*, **91**, 41046s (1979).
8. N. Okubo, I. Shirahata, and N. Kitamura, heat-resistant polyurea urethane resin coating compositions, Jpn. Kokai 77, 59,632 (1977); *Chem. Abstr.*, **87**, 119386s (1977).
9. Y. Ide, T. Nishizawa, Y. Kanai, and Y. Yamazaki, polyurethane insulating varnishes, Jpn. Kokai 76, 133,328 (1976); *Chem. Abstr.*, **86**, 91884f (1977).
10. M. Hayashizaki, M. Nakano, Y. Sone, and H. Kawashima, polyurethane insulating varnishes, Jpn. Kokai 75, 88,129 (1975); *Chem. Abstr.*, **84**, 19294e (1976).
11. E. Hosokawa, T. Hoshino, M. Waki, M. Fukushima, and K. Asada, insulating varnishes, Jpn. Kokai 77, 36,134 (1977); *Chem. Abstr.*, **87**, 54219t (1977).
12. K. Takizawa and T. Ito, polyurethane electric insulating coatings, Jpn. Kokai 74, 92,145 (1974); *Chem. Abstr.*, **82**, 87772t (1975).
13. Y. Okada, S. Kasai, and M. Nakano, electrically insulating polyurethane coating materials for wires, Jpn. Kokai 77, 123,432 (1977); *Chem. Abstr.*, **88**, 122782u (1978).

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