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Properties of Poly[N,N′-(4,4′-diphenyl ether) 4-Amidophthalimide] Film

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Synopsis

A high molecular weight polyamide–imide polymer derived from the reaction of TMAC–DAPE has been prepared and its film properties have been evaluated. Poly-[N,N′-(4,4′-diphenyl ether) 4-amidophthalimide] film has an excellent combination of mechanical, electrical, and chemical properties at room temperature and at 200°C. A comparison of the film properties of this material with those of a commercial polyimide film, Teflon, FEP, Nomex paper, and Mylar films is also presented.

INTRODUCTION

For the past several years we have been engaged in the evaluation of high-temperature polymers, particularly the class of polymers known as the polyamide–imides. An excellent review and bibliography on this subject has been presented elsewhere.[1,2] These polymers are prepared by the polycondensation reaction between a trimellitic anhydride–acid chloride and an aromatic diamine. As a class, these polymers possess a unique combination of properties and retain a good percentage of these properties from room temperature to 500°F. They have excellent resistance to radiation, chemicals, water, abrasion, as well as high thermal stability, good mechanical properties, and excellent electrical properties. This article discusses one of these polyamide–imides, specifically, the one derived from 4-chloroformylphthalic anhydride and 4,4′-diaminodiphenyl ether. The polymerization and conversion reactions for this polymer are described in a previous paper.[3]

EXPERIMENTAL

Test Methods

The mechanical and electrical properties of the polymer film were measured according to prescribed ASTM methods and are identified in Table I. The mechanical properties of the film are affected by processing conditions, and, therefore, a range of property values are shown. Density was measured in a benzene–carbon tetrachloride system at 24°C. Chemical resistance in selected media was determined by immersing the film for 48 hr and visually inspecting the sample.

TABLE I
Comparison of Film Properties[a]

Property	Temp., °C	Amide–imide	Mylar[b]	Nomex[b]	Kapton[b]	Teflon FEP[b]	Test method
Tensile strength, psi	25	15,000–21,000	23,000	12,000	25,000	3,000	ASTM D882
	200	7,800–9,300	7,000	8,500	17,000	400	
Elongation, %	25	10–60	100	10	70	300	ASTM D882
	200	10–25	>100	8	90		
Tensile modulus, psi	25	$0.35–0.50 \times 10^6$	0.55×10^6	0.2×10^5	0.43×10^6	0.43×10^5	ASTM D882
	200	0.32×10^6	0.05×10^6		0.26×10^6	0.2×10^4	
Fold Endurance, cycles	25	20,000–500,000	14,000		500,000	4,000	ASTM D2176 (1 kg)
Tear Strength, g/mil	25	450	600		510	125	ASTM D1004
Density, g/cc		1.39	1.39	0.90	1.43	2.15	
H_2O absorption, %		2.5	<1	6	2	0.01	24 hr–100°F–100% R.H.
Dielectric strength, kV/m	25	4–6.5	7	0.450	7	7	ASTM D149 (60 Hz)
	200	4	5[c]		5.6		
Dielectric constant	25	3.5	3.1	2.0	3.5	2.0	ASTM D150 (1 KHz)
	200	4.0		2.3	3.0		
Dissipation factor	25	0.008	0.005	0.02	0.003	0.0002	ASTM D150 (1 KHz)
	200	0.018	0.01	0.01	0.002		
dc Volume Resistivity	25	10^{16}	10^{18}	10^{13}	10^{18}	10^{19}	ASTM D257
(500 volts), ohm-cm	200	10^{12}	10^{11}		10^{14}		
UV resistance							
dry		fair	fair		fair	—	FS/BL exposure
wet		poor	—		poor	good	Weatherometer
Chemical resistance							
benzene, toluene		OK	OK	OK	OK	OK	48 hr immersion at room temperature
methanol		OK	OK	OK	OK	OK	
p-cresol		OK	OK	OK	OK	OK	
DMAC, NMP, DMF		OK	OK	partially dissolves	OK	OK	
NaOH 4%		OK	OK	OK	degrades	OK	70 hr at room temp.

[a] Film thickness, 1 mil, except amide–imide, which is 1.3 mils.
[b] Registered trademarks of E. I. du Pont Co.
[c] At 150°C.

Preparation of Films

A thin layer (10–20 mils) of the precursor solution is doctored onto either glass or metal substrates and dried to 150°C over a $^1/_2$-hr period. The partially cured film is then removed from the substrate, clamped on a suitable frame, and cured to 300°C over a period of about $^1/_2$ hr. Film thickness ranged from 1 to 2 mils.

RESULTS AND DISCUSSION

The properties of this amide–imide polymer approach those of the polyimide polymer identified under the trade name of Kapton. The highly aromatic character of this polymer contributes to its good thermal properties, and at the same time, the presence of the amide group contributes to its ease of processing, toughness, and flexibility. These characteristics, combined with high electrical resistance, low dielectric loss, and high electrical breakdown strength, provide a new dielectric material with an excellent combination of properties. Table I summarizes the film properties of the polymer from TMAC–DAPE. The properties of several other film materials and of Nomex paper are also shown for comparison.[4,5] The film is transparent and light amber in color. Because half of the polymer is composed of amide groups, some difference in the properties is to be expected when compared to the commercial polyimide polymer. At elevated temperatures, the mechanical properties of this amide–imide film are still quite good. In fact, the tensile strength at 200°C is better than the strength that many films have at room temperature. The tensile properties of this amide–imide film are shown in Table II.

At about 200°C, the elongation begins to show a marked increase until it peaks at 300°C. During this interval, the modulus of the film decreases by 90%. These data are shown graphically in Figure 1 to better illustrate the slope changes in the property curves. This particular set of data applies to a film sample that had a previous cure temperature cycle from 100° to 275°C.. This temperature is below what is believed to be the optimum cure temperature of 300–325°C. It is possible that the property curves for a completely cured film would be shifted slightly toward higher values.

TABLE II
Mechanical Properties Versus Temperature

Temp., °C	Tensile strength, psi	Tensile Modulus $\times 10^5$, psi	Elongation, %
R.T.	18,500	5.0	30
100	14,250	4.1	26
200	7,825	3.2	25
250	4,650	1.5	39
300	1,625	0.2	61
350	995	0.1	36
400	506	0.1	9

TABLE III
Electrical Properties of Amide–Imide Film Cured to Various Temperatures

Property	190°C	240°C	260°C	300°C	325°C
Dielectric strength, kV/mil	5.1	5.0	5.7	5.3	5.7
Dissipation factor	0.018	0.010	0.007	0.008	0.008
dc Volume resistivity, ohm-cm	1.9×10^{14}	7.2×10^{15}	3.1×10^{15}	8.3×10^{15}	1.5×10^{16}

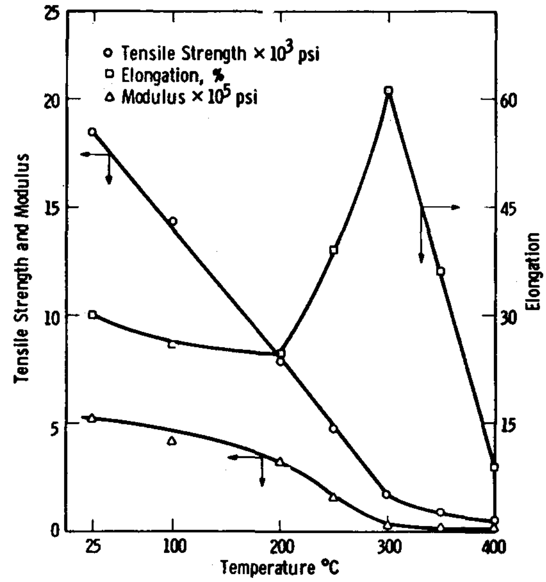


Fig. 1. Mechanical properties vs. temperature of poly[N,N′-(4,4′-diphenyl ether) 4-amidophthalimide] film.

Electrical Properties

The electrical properties of polymers depend more on an unbalance or asymmetry of dipoles than on the presence of polar groups per se. Unlike the polyimide Kapton, the polyamide–imide molecule is not symmetrical and one would expect to find slightly higher electrical properties (dissipation factor and dielectric constant) (see Table I). While these properties reflect the asymmetry of the amide–imide molecule, the electricals are quite good, even at elevated temperature. Optimum electrical properties are obtained only after conversion of the amic acid precursor to the amide–imide is essentially complete. Data showing the electrical properties of film measured at room temperature and cured to various temperatures are shown in Table III.

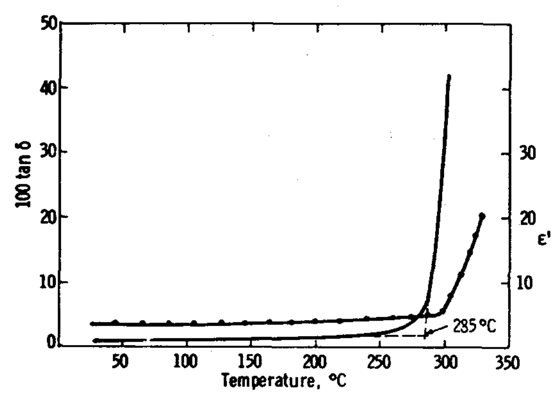
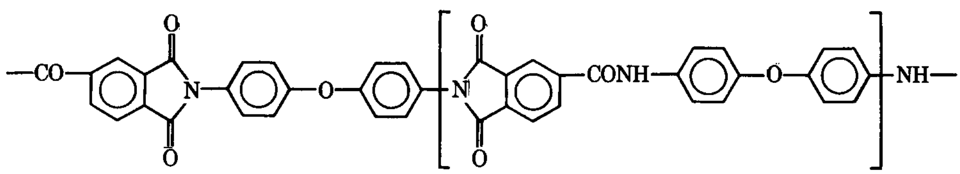


Fig. 2. Dielectric constant ϵ' and dissipation factor tan δ as a function of temperature at 10^3 Hz: (-●-) ϵ'; (—) tan δ.

The dielectric constant (ϵ') and the dissipation factor (tan δ) for this amide–imide film are shown as functions of temperature in Figure 2. ϵ' is about 3.5 at room temperature and remains constant up to about 225°C, at which point it begins to rise slowly until about 300°C where a marked change in slope occurs. The dissipation factor behaves in a similar fashion except that this change in slope occurs at a slightly lower temperature.

Plots of tan δ versus temperature have been used to estimate the glass transition temperatures (T_g) of various polymers. Freeman et al.[7] as well as Cooper et al.[8] have determined the T_g of several high-temperature polyamides and polyimides. From the curve shown in Figure 2, we estimate a T_g of about 285°C. This approximation is consistent with a value of 285°C reported by Wrasidlo and Augl[9] for an amide–imide of the structure shown below. That portion of the structure within the brackets represents the polyamide–imide described in this paper:



Further evidence suggesting a T_g of about 285°C is obtained from DTA measurements. A small endotherm occurs at 282°C on the DTA curve which is indicative of a phase change in the polymer.

Chemical Resistance

Samples of the polyamide–imide film were immersed in various chemical solutions and were examined for any changes in appearance. These results are shown in Table I along with comparative data on other film materials. In addition, film samples of the amide–imide and Kapton materials were immersed in 4% NaOH solution for 24 and 70 hr at 75–80°F. After this period, the Kapton film became jelly-like and translucent and was quite sticky. No sign of attack was apparent on the amide–imide film. The tensile and elongation properties of both films were measured after the 24-hr immersion period. These results are shown in Table IV.

TABLE IV
Chemical Resistance of Films Immersed in NaOH

	Thickness before, mils	Thickness after, mils	Tensile strength, psi	% Change	Elongation, %	% Change
Amide–imide control	1.5	—	18100	—	29	—
Amide–imide exposed	—	1.5	18825	+4%	24	−17%
Kapton control	1.1	—	19500	—	20	—
Kapton exposed	—	0.7	17525	−10%	13	−35%

CONCLUSIONS

An amide–imide polymer derived from the reaction of TMAC–DAPE has been evaluated and shown to possess an excellent combination of mechanical, electrical, and chemical properties. The film properties are quite good at room temperature and at elevated temperatures.

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