Synthesis and characterization of elastomer-modified polyimide films

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A study has been conducted to determine the effects of added elastomers on the film properties of a linear aromatic polyimide. Polyamic acids have been prepared via reaction of BTDA (3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride) with ODA (4,4′-oxydianiline) and various ATBN (aromatic amine-terminated butadiene acrylonitrile) elastomers. Films were prepared and thermally converted to the corresponding polyimides. Optimum cure conditions for BTDA+ODA/ATBN films were evaluated. The effect of elastomer concentration on BTDA+ODA thermal properties, density, tensile properties, morphology and tear resistance were evaluated. Variation of the acrylonitrile content of the ATBN elastomer in BTDA+ODA was performed and properties evaluated. Incorporation of ATBN into BTDA+ODA caused a decrease in the glass transition temperature, thermal stability, tensile strength and modulus of films. Increases of film tear resistance were observed for several formulations of ATBN in the BTDA+ODA polyimide.

(Keywords: polyimides; elastomer modification; polyimide film; tear strength; microphase separation; aromatic amine-terminated butadiene acrylonitrile elastomer)

INTRODUCTION

Linear aromatic condensation polyimides are materials of prime choice for use as films and coatings on advanced spacecraft and aircraft where durability at temperatures in the range of 200–300°C is required. Linear polyimides are particularly attractive for applications on large antennae or space structures because of their inherent toughness, flexibility, low density, thermal stability and radiation resistance over a broad temperature range. A drawback which limits the use of polyimide films for the above-mentioned applications in space is the tendency to tear upon impact from space debris, meteors, etc. Elastomers have been incorporated into linear polyimide film in the present investigation with the goal of improving film tear resistance, and thereby increasing the potential of such films for use in a space environment.

The introduction of elastomeric segments into polyimides has previously been performed to improve properties such as fracture toughness, impact strength and processability. These modifications were generally made with the desire to maintain the excellent thermal properties of the polymer. Both addition[1–4] and linear[5–7] polyimides have been modified by the addition of silicone and ATBN (amine-terminated butadiene acrylonitrile) elastomers. In this investigation, the effect of incorporation of aromatic ATBN elastomers into a polyimide derived from 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA) and 4,4′-oxydianiline (ODA) was studied. Variations in the amount and acrylonitrile composition of the rubber were studied with regard to effects on the glass transition temperature, thermal stability, mechanical properties and teart resistance of the polyimide films.

EXPERIMENTAL

Materials

The materials used to prepare the polymers of this investigation are shown in *Figure 1*. The 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA) was obtained from commercial sources, recrystallized from anisole/acetic anhydride and sublimed at 215°C and less than 1 torr pressure prior to use; m.p. 285°C. The 4,4′-oxydianiline (ODA) was recrystallized from ethanol/water, then sublimed at 160°C and less than 1 torr pressure; m.p. 188–190°C (dec.). The aromatic amine-terminated butadiene acrylonitrile (ATBN) elastomers were experimental materials obtained from the B. F. Goodrich Research Center, Brecksville, Ohio, and used as received. The elastomer containing 18% by weight acrylonitrile (ATBN$_{18}$) had an amine equivalent

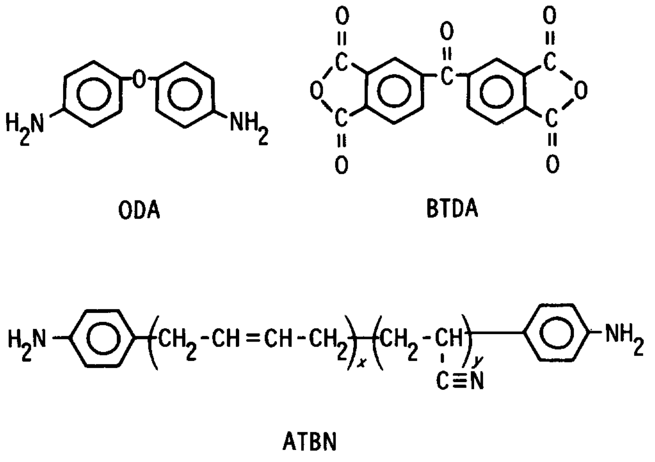
ODA
BTDA
ATBN

Figure 1 Starting materials

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weight (NH_2) of 746; the elastomer containing 10% acrylonitrile ($ATBN_{10}$) had an amine equivalent weight of 765; and that containing no acrylonitrile ($ATBN_0$) had an amine equivalent weight of 928. The *N*,*N*-dimethylacetamide (DMAc) was obtained from commercial sources, and used as received.

Polymer synthesis

Two different methods were used for the synthesis of BTDA + ODA/ATBN polyamic acids owing to the varying solubilities of elastomer in DMAc. BTDA + ODA polyamic acids containing elastomer with acrylonitrile content of 18% ($ATBN_{18}$) were synthesized by mechanically stirring $ATBN_{18}$ in DMAc until dissolved. The ODA was then added and stirred until dissolved. The BTDA was added to the diamine solution in the amount necessary for a 1:1 amine:anhydride stoichiometry, and the solution stirred until all monomers had dissolved to produce a viscous yellow translucent resin. The final polyamic acid solution concentrations were 15% solids. BTDA + ODA polyamic acids prepared with ATBN elastomers containing 0% ($ATBN_0$) and 10% ($ATBN_{10}$) acrylonitrile were prepared by first swelling the ATBN with 15% (w/w) *m*-xylene, then adding DMAc and stirring. The ODA and BTDA were then added to the elastomer as before for an overall concentration of 15% solids. Solutions were stirred for 3–4 h, then frozen until used for film fabrication.

Film preparation

BTDA + ODA/ATBN polyamic acids were centrifuged at approximately 500 rpm before film casting. Solutions were poured onto acid-cleaned, dust-free soda-lime glass plates and spread with a doctor blade using a 0.0025 cm blade gap in order to obtain films with a final thickness of 1 mil (0.001 inch). The films were allowed to dry for 3–4 h at room temperature, then thermally treated for further solvent removal and final conversion of the polyamic acid to the polyimide in an air or nitrogen environment for 1 h each at 100, 200 and 250 or 300°C. Thermal treatment at 300°C and cure in an air environment were found to be detrimental to final film properties and will be discussed later in detail. After cooling to room temperature, the polyimide films measuring approximately 1.0 mil in thickness were removed from the glass plates by soaking in water.

Polymer characterization

Inherent viscosities of the BTDA + ODA/ATBN polyamic acids were measured at 35°C in DMAc at a concentration of 0.5% (w/w). Softening temperatures (T_g) of polyimide films were measured by thermomechanical analysis (t.m.a.) on a DuPont 943 thermomechanical analyser at 5°C min^{-1} in static air. Thermograms of the films were obtained using thermogravimetric analysis (t.g.a.) at 2.5°C min^{-1} in flowing air (15 cm^3 min^{-1}). Torsional braid analysis (t.b.a.) was used to obtain thermomechanical properties of the BTDA + ODA/ATBN resins. Polyamic acid/DMAc solutions (10% w/w) were coated onto glass braids and preheated in a nitrogen oven for 1 h each at 100, 200 and 250 or 300°C. T.b.a. were recorded on heating at 3°C min^{-1} from room temperature to 400°C and cooling to cryogenic temperatures. Infrared (i.r.) spectra were obtained on a Perkin–Elmer model 297 infrared spectrometer. Film density values were obtained using a Techne density gradient column, and represent averages of two or three measurements. Film tensile data were obtained with film samples (2.54 × 15.24 by 0.0025 cm thick) on an Instron Universal Testing Instrument equipped with a quartz lamp heater. A 0.05 cm min^{-1} crosshead speed was used. Testing of samples at elevated temperature was performed after a 10 min soak at the test temperature. All data represent averages of 8–10 individual specimens.

Scanning electron microscopy (SEM) was performed on the fracture surfaces of films torn at room temperature. Samples were gold-coated via vapour deposition to alleviate charging, and examined in a Cambridge Instruments Stereoscan 150 SEM at an accelerating voltage of 20 kV.

Transmission electron microscopy (TEM) was performed by the Virginia Institute of Marine Science, Gloucester, VA. Film samples were prepared as follows. Films were first embedded in Epon 812, then thin-sectioned after hardening of the resin. The sections were mounted on 300 mesh gold grids which were then dipped into a 1% OsO_4 solution in tetrahydrofuran for 45 s for the purpose of staining the elastomer segments[8]. Samples were rinsed in methanol and 0.22 μm filtered water for 5–10 s each and dried in air. The film sections were then examined with a Hitachi model HV-11B transmission electron microscope.

Volume fractions of elastomer particles were determined by tracing transmission electron micrographs of the osmium-stained, microtomed thin sections onto a graph-paper grid[9]. Only two micrographs of each composition were available; however, volume fraction determinations for the two photos agreed well. For comparison, calculations of expected volume fractions were made by assuming volume additivity and densities of 0.92, 0.94 and 0.96 for the elastomers containing 0, 10 and 18% acrylonitrile respectively.

Tearing force measurements were made using the single-tear 'trousers' testpiece[10]. The specimens were reinforced with pressure-sensitive tape on either side of the central crack path. Without this modification, the tear would frequently run to the edge of the specimen, whereas use of reinforcing tape allowed measurements to be made along the entire specimen length. Care was necessary, however, to centre the crack between the tape strips, since higher forces were observed when the tear propagated along the edge of the tape. A single specimen of each composition was tested, yielding 10–20 data points at varius tearing rates.

Sectioning of the torn pieces perpendicular to the crack revealed that the fracture surfaces lay at approximately 45° to the plane of the film; reported tearing energies were calculated relative to the area torn through as $T = 2F/(2^{\frac{1}{2}}t)$, where F is the tearing force and t is the film thickness. Tearing force varied approximately linearly with log(crosshead speed) over the range 0.051 to 5.1 cm min^{-1}, although the dependence was not strong. Comparisons between films were made at a reference speed of 0.51 cm min^{-1}.

RESULTS AND DISCUSSION

Optimum cure determination

The BTDA + ODA/$ATBN_{18}$ resin was used to determine optimum cure conditions for the preparation

Table 1 BTDA+ODA with 15% $ATBN_{18}$–cure parameters

Cure	T.m.a. T_g (°C)	T.g.a. at 10% wt loss (°C)	Appearance
Air/300°C	280	493	Brown, clear
N_2/300°C	281	490	Light yellow, translucent
Air/250°C	258	470	Dark yellow, translucent
N_2/250°C	269	504	Light yellow, translucent

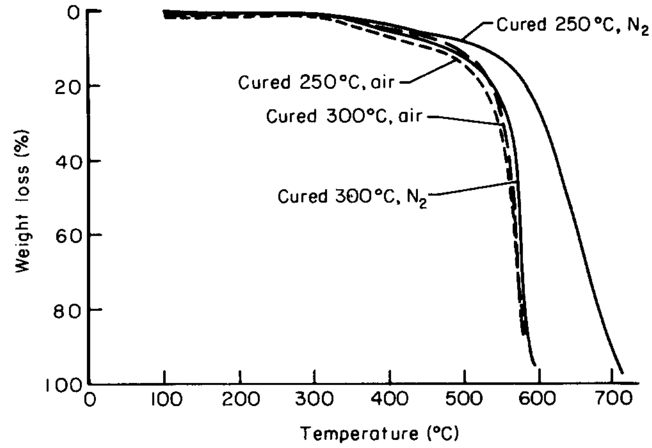

Figure 2 T.g.a. of BTDA+ODA films containing 15% $ATBN_{18}$

of ATBN elastomer-modified films. It was necessary to find an optimum temperature and atmosphere which would complete imidization without decomposing the more thermally sensitive elastomer. Thermal data and appearance of films prepared under the different cure conditions are noted in *Table 1*. BTDA+ODA/$ATBN_{18}$ films cured in air were dark in colour relative to films cured in N_2 which were light yellow (as is BTDA+ODA containing no ATBN). Oxidative degradation of the elastomer due to the presence of air is no doubt responsible for this darkening effect. T.g.a. profiles of BTDA+ODA/$ATBN_{18}$ are shown in *Figure 2*. The best thermal stability is displayed by the 250°C N_2-cured film. *Figure 3* exhibits the t.b.a. spectra of films prepared using different cure conditions. Glass transitions (T_g) are observed at approximately −90°C and 300°C for the $ATBN_{18}$ elastomer and polyimide respectively. The $ATBN_{18}$ peak is somewhat diminished in the case of the 300°C air-cured polymer, indicating loss or alteration of the elastomer during cure. The $ATBN_{18}$ peak is observed in the t.b.a. spectra of materials prepared under the other three cure conditions. The T_g of neat $ATBN_{18}$ was observed to be −39°C via t.b.a. (not shown). The T_g of $ATBN_{18}$ is apparently lowered after incorporation into polyimide. The reason for this effect is unclear, although it has been experienced before[1] upon modification of addition polyimide adhesives with $ATBN_{18}$. It is possible that, after heating to 400°C in nitrogen on the t.b.a. apparatus, the rubber began to decompose. Infrared spectra of a 300°C air-cured film, a 250°C N_2-cured film, a BTDA+ODA control film and the neat $ATBN_{18}$ are presented in *Figure 4*. Noticeable differences between the two BTDA+ODA/$ATBN_{18}$ films are seen at 2930, 2845, 2240 and 968 cm^{-1}. Lower absorption at 2930 and 2845 cm^{-1} in the spectrum of the 300°C air-cured film can be ascribed to loss of aliphatic hydrogen, probably due to decomposition of the elastomer. The elastomer nitrile peak at 2240 cm^{-1} is also absent after 300°C air curing.

These experiments indicated that a 250°C N_2 cure produced BTDA+ODA/$ATBN_{18}$ films with good thermal stability and little or no decomposition of the $ATBN_{18}$. Therefore, all ATBN-containing films prepared for further characterization in this study were cured at 250°C in N_2.

Effect of elastomer concentration on film properties

The BTDA+ODA/$ATBN_{18}$ system was selected for a study in which the $ATBN_{18}$ content was varied in order to determine concentration effects on polymer solution and film properties. Concentrations of 0, 5, 10, 15 and 20% (w/w) $ATBN_{18}$ in BTDA+ODA were prepared and polymer solution/film properties evaluated.

Polymer solution/film properties as a function of $ATBN_{18}$ concentration are shown in *Table 2*. All solutions prepared had inherent viscosities of at least 0.99 dl g^{-1}. Density of the BTDA+ODA/$ATBN_{18}$ films decreased gradually with increasing $ATBN_{18}$ content to 15% concentration, where a limiting value apparently was reached. The glass transition temperature T_g (via t.m.a.) was depressed by introduction of $ATBN_{18}$. BTDA+ODA thermal decomposition was apparently unaffected by concentrations of 5 or 10% $ATBN_{18}$. Decreases in thermal stability of BTDA+ODA were experienced for concentrations of 15 and 20% $ATBN_{18}$. No doubt the aliphatic component of the $ATBN_{18}$ was contributing to this enhanced decomposition. However,

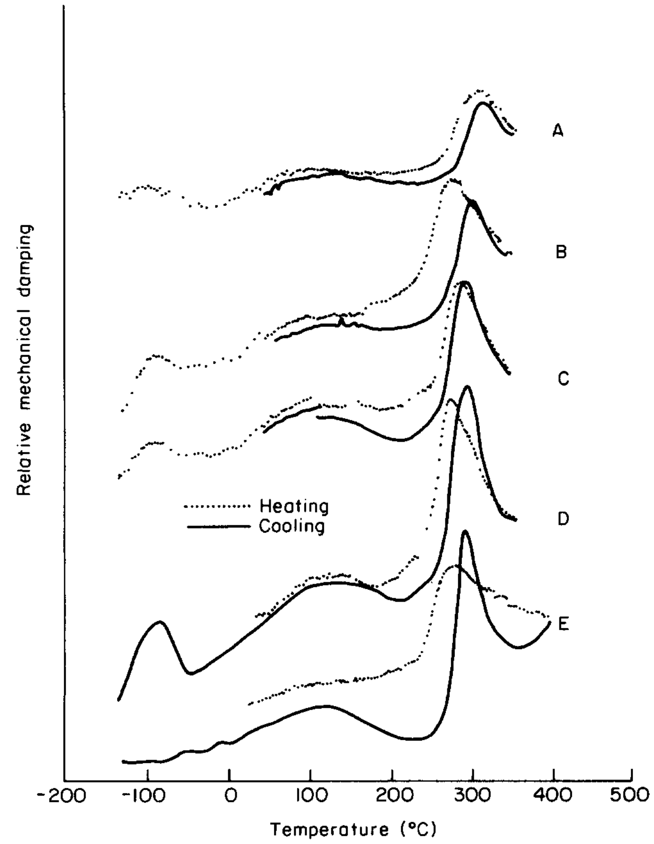

Figure 3 T.b.a. spectra of BTDA+ODA containing 15% $ATBN_{18}$ cured 300°C, air (A); 250°C, air (B); 300°C, N_2 (C); 250°C, N_2 (D); and BTDA+ODA control cured 250°C, N_2 (E)

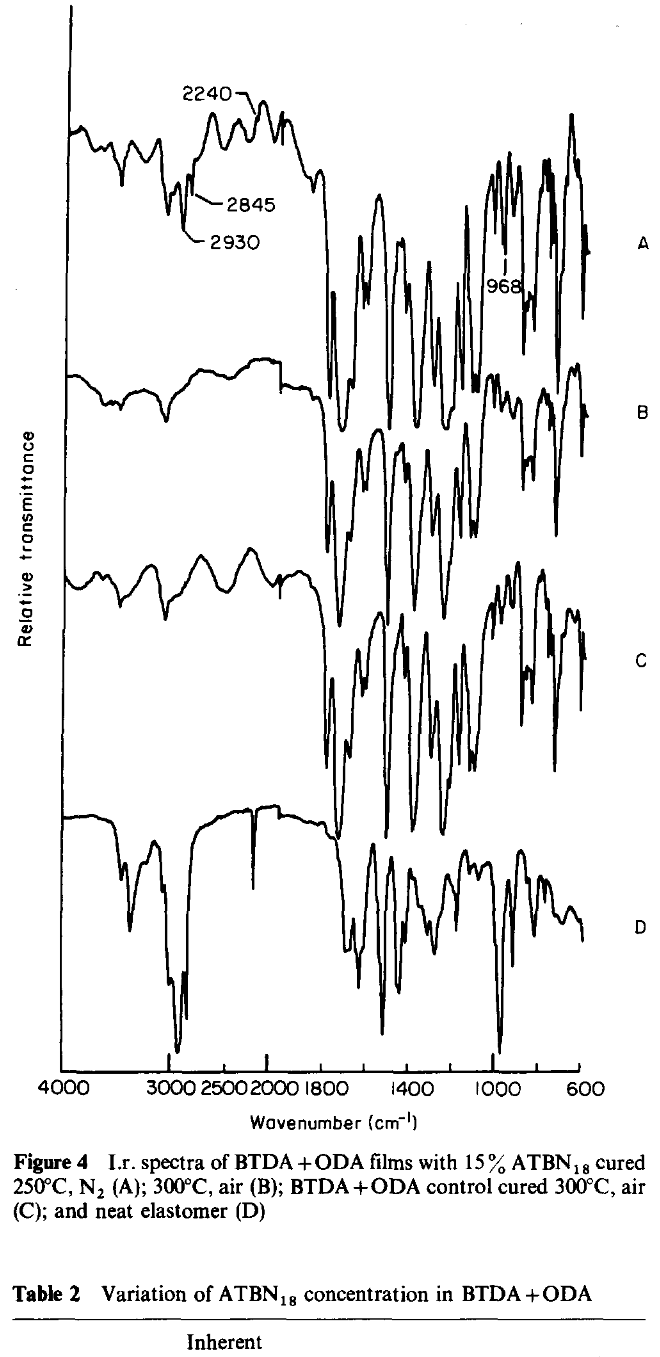

Figure 4 I.r. spectra of BTDA+ODA films with 15% $ATBN_{18}$ cured 250°C, N_2 (A); 300°C, air (B); BTDA+ODA control cured 300°C, air (C); and neat elastomer (D)

Table 2 Variation of $ATBN_{18}$ concentration in BTDA+ODA

Concentration (% w/w) ATBN	Inherent viscosity (dl g^{-1})	T.m.a. T_g (°C)	T.g.a. (°C) at 10% wt loss	Density (g cm^{-3})
0	1.48	281	538	1.382
5	0.99	274	540	1.355
10	1.52	274	536	1.259
15	1.72	270	504	1.237
20	2.21	264	492	1.238

this contribution was not dramatic; the worst case was the 20% $ATBN_{18}$ preparation with a 10% weight loss temperature of 492°C.

Films containing 0, 5, 10, 15 and 20% $ATBN_{18}$ were examined by TEM (*Figures 5–9*). It is evident that phase separation has occurred in all the $ATBN_{18}$-containing samples, resulting in formation of the elastomeric domains pictured. *Figure 5* (0% ATBN) exhibits no such features. Domain size appears to increase with $ATBN_{18}$ concentration. Most of the $ATBN_{18}$-containing materials exhibit a variety of particle sizes. The lowest detectable particle size is about 0.1 μm, ranging to about 5 μm in the 15% and 20% $ATBN_{18}$ films. This particle size range from 0.1 to 5.0 μm (10^3–10^4 Å) coupled with the fact that all of the ATBN-containing polyimides displayed two separate and distinct glass transition temperatures characteristic of each component would lead us to believe that these systems are block copolymers displaying supermolecular structure behaviour.

Table 3 shows the results of an analysis of the TEM photos. In each case, except the film containing 20% rubber, a sizable percentage of the added elastomer is unaccounted for in the observed domains, which means that it is either molecularly dispersed in the continuous phase or present as particles smaller than 0.1 μm (which

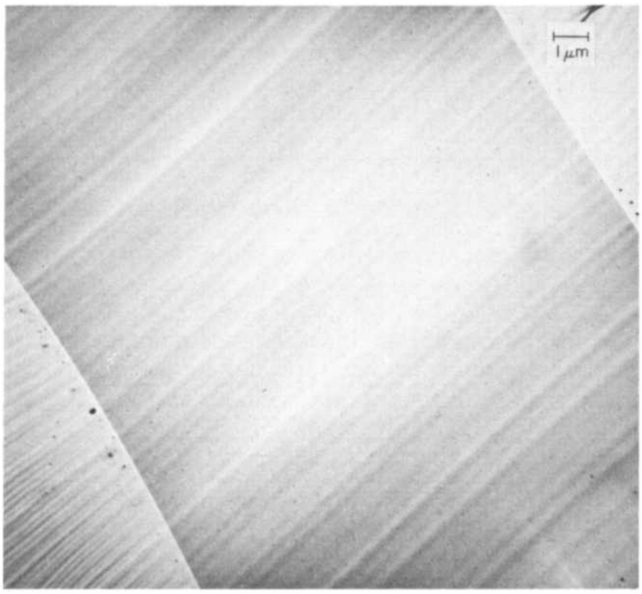

Figure 5 TEM of BTDA+ODA

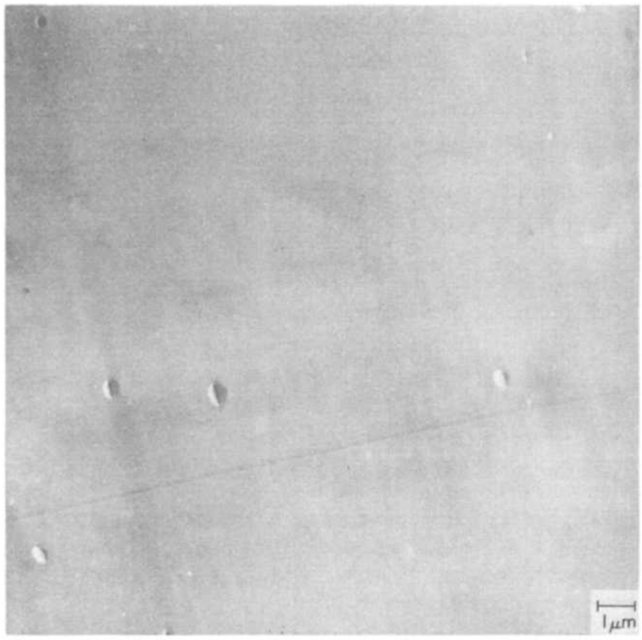

Figure 6 TEM of BTDA+ODA 5% $ATBN_{18}$ film

Figure 7 TEM of BTDA+ODA 10% $ATBN_{18}$ film

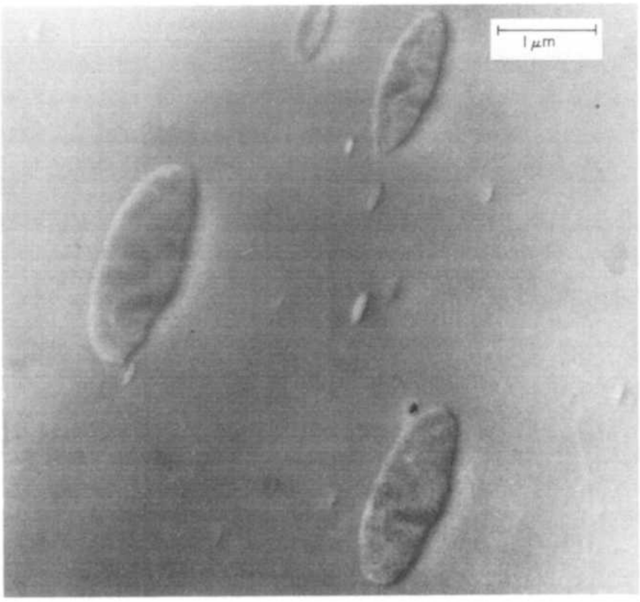

Figure 8 TEM of BTDA+ODA 15% $ATBN_{18}$ film

was the smallest size counted in analysing the photomicrographs). The amount of this highly dispersed elastomer is generally 5–10%.

Tensile data obtained on BTDA+ODA with various concentrations of $ATBN_{18}$ are shown in *Table 4*. Average deviations ranged from 6 to 10% for both room-temperature and 200°C tensile data. Room-temperature yield strength, tensile strength and tensile modulus generally decreased with increasing $ATBN_{18}$ content. The 20% $ATBN_{18}$-containing material was somewhat anomalous in exhibiting higher yield strength, tensile strength and tensile modulus than the 15% $ATBN_{18}$ film. This anomaly did not appear at 200°C. At 200°C, increasing $ATBN_{18}$ content gave decreasing yield strength, tensile strength and tensile modulus. The decreases in modulus with increasing content of soft elastomeric segments might have been expected, no matter what morphology the polymers assumed. In light of the phase separation observed in the TEM, however, it

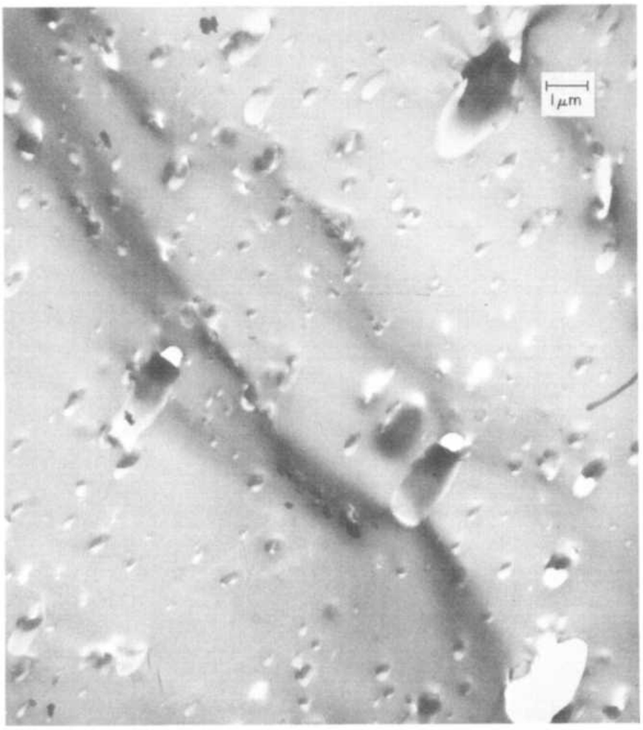

Figure 9 TEM of BTDA+ODA 20% $ATBN_{18}$ film

Table 3 Rubber volume fractions

BTDA+ODA	Rubber added (vol %)	Observed particles (vol %) by TEM
0% $ATBN_{18}$	0	–
5% $ATBN_{18}$	7.0	0.9
10% $ATBN_{18}$	13.8	9.6
15% $ATBN_{18}$	20.3	8.5
20% $ATBN_{18}$	26.5	25.0
15% $ATBN_0$	21.0	–
15% $ATBN_{10}$	20.6	14.0

Table 4 Effect of $ATBN_{18}$ concentration on tensile properties

ATBN (%)	Yield strength at 2%, MPa (psi)		Tensile strength, MPa (psi)		Tensile modulus, MPa (ksi)	
	RT	200°C	RT	200°C	RT	200°C
0	60.7 (8800)	38.6 (5600)	105.5 (15300)	45.5 (6600)	3000 (440)	1600 (231)
5	61.4 (8900)	37.9 (5500)	85.5 (12400)	46.2 (6700)	2700 (390)	1600 (233)
10	53.8 (7800)	31.0 (4500)	82.7 (12000)	34.5 (5000)	2100 (303)	1300 (186)
15	49.6 (7200)	25.5 (3700)	76.5 (11100)	31.7 (4600)	2000 (289)	1200 (168)
20	51.0 (7400)	22.8 (3300)	82.0 (11900)	27.6 (4000)	2300 (328)	900 (128)

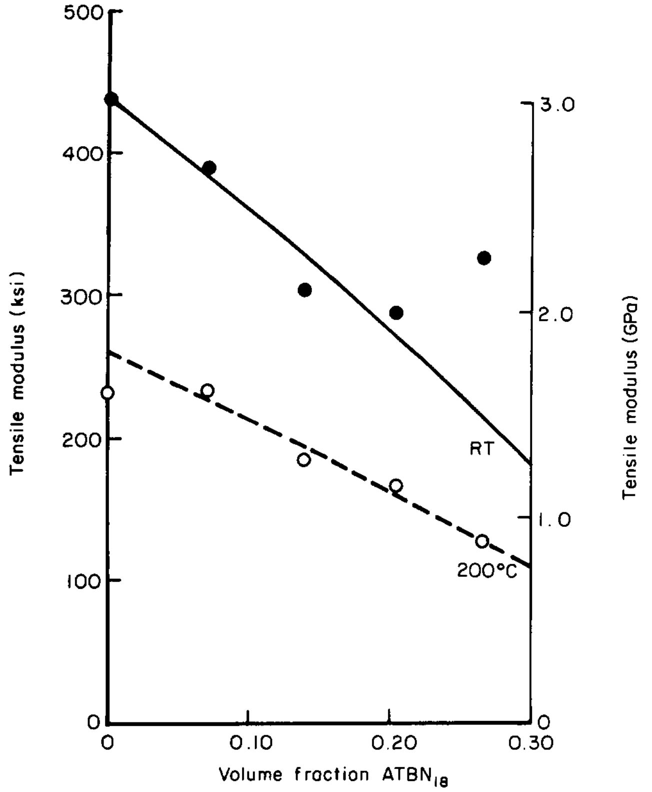

Figure 10 Tensile modulus vs. volume fraction of $ATBN_{18}$. Filled circles: room-temperature data. Open circles: 200°C data. Lines are calculated using the polyaggregate model with the following parameters: $E_1 = 440$ ksi (RT), $E_1 = 260$ ksi (200°C); E2 = 440 psi; $v_1 = 0.35$; $v_2 = 0.49$; where E and v are Young's modulus and Poisson's ratio respectively, and the subscripts refer to phases 1 and 2

Table 5 Variation of elastomer acrylonitrile content in BTDA + ODA containing 15% ATBN

Acrylonitrile (%)	Inherent viscosity ($dl\,g^{-1}$)	T.m.a. T_g (°C)	T.g.a. at 10% wt loss	Density ($g\,cm^{-3}$)	Appearance
0	0.88	272	490	1.252	Yellow, opaque
10	0.83	269	470	1.266	Yellow, opaque
18	1.72	270	516	1.237	Light yellow, translucent

is tempting to go further and to attempt to model the films as composites in which the continuous phase ('matrix') is BTDA + ODA and the dispersed phase ('filler') is ATBN elastomer. When this is done, using the self-consistent solution of Kerner[11], the model consistently overestimates the moduli of the rubber-containing films. Dickie[12] has reviewed various modifications which have been made to this model in order to improve the fit. However, another model, also due to Kerner, has been used very successfully to predict the moduli of block copolymers[13]. This packed-grain or 'polyaggregate' model is compared with our experimental moduli in *Figure 10*, and the fit seems quite good. In order to achieve this fit, a value for the modulus at 0% elastomer had to be estimated by sketching a smooth curve through the data. Ranges of the three other model parameters were chosen to be generally typical of glassy and rubbery polymers, respectively. Fortunately, calculation showed that these other parameters do not need to be known with great precision.

The relative success of this model, compared to one which assumes only discrete rubber particles in a hard matrix, is consistent with the proposal that there is some phase mixing in these films.

Effect of acrylonitrile content on film properties

Solution/film properties of BTDA + ODA containing 15% ATBN with acrylonitrile contents of 0, 10 and 18% are presented in *Table 5*. Solutions of polymers containing $ATBN_0$, $ATBN_{10}$ and $ATBN_{18}$ displayed high inherent viscosities ($\eta_{inh} \geqslant 0.83$) and produced flexible films. Variation in acrylonitrile content had no effect on T_g and little effect on the densities of the BTDA + ODA/ATBN films. A noticeable decrease in thermal stability was obtained when amount of acrylonitrile in ATBN was decreased from 18% to 10% or 0%. The worst case was the BTDA + ODA/$ATBN_{10}$ film, with a 10% weight loss temperature of 470°C, 46°C lower than for the $ATBN_{18}$ film.

Tensile properties of the BTDA + ODA films containing 15% ATBN with varying concentrations of acrylonitrile are shown in *Table 6*. Average deviations ranged from 7 to 11%. Room-temperature yield strengths of $ATBN_{10}$ and $ATBN_{18}$ are identical, with the $ATBN_0$ film 9% lower in value. Room-temperature tensile strengths range from 75.8 to 79.3 MPa. Room-temperature tensile modulus is highest for the $ATBN_0$-derived material (2100 MPa) and lowest for the $ATBN_{10}$ material (1900 MPa). At 200°C all tensile properties are much diminished. For this concentration of elastomer (15% w/w), marginal improvement of tensile properties was realized via incorporation of the $ATBN_0$ elastomer relative to the $ATBN_{10}$ and $ATBN_{18}$.

Figures 11, *12* and *13* are SEM micrographs of fractured edges of BTDA + ODA films containing 15% $ATBN_0$, $ATBN_{10}$ and $ATBN_{18}$. In all cases, SEM of these fracture edges reveals microphase separation. A greater degree of phase separation appears to have occurred within the $ATBN_0$ and $ATBN_{10}$ films than the $ATBN_{18}$ film. Analysis of the available TEM photos of the $ATBN_{18}$- and $ATBN_{10}$-containing films had also suggested that the former is more highly dispersed (*Table 3*). This is probably due to the lower solubility of the $ATBN_0$ and $ATBN_{10}$ elastomers, relative to the $ATBN_{18}$.

Tear data. Tear energies are collected in *Table 7*. It may be seen that, as the content of high-nitrile rubber is increased, tear energies go through a broad maximum, with a peak at 15% rubber by weight. The single highest

Table 6 Effect of acrylonitrile content on tensile properties of BTDA + ODA films containing 15% ATBN

Elastomer acrylonitrile (%)	Yield strength at 2%, MPa (psi)		Tensile strength, MPa (psi)		Tensile modulus, MPa (ksi)	
	RT	200°C	RT	200°C	RT	200°C
0	45.5 (6600)	30.3 (4400)	79.3 (11500)	33.8 (4900)	2100 (302)	1200 (167)
10	49.6 (7200)	24.8 (3600)	75.8 (11000)	29.0 (4200)	1900 (269)	1000 (146)
18	49.6 (7200)	25.5 (3700)	76.5 (11100)	31.7 (4600)	2000 (289)	1200 (168)

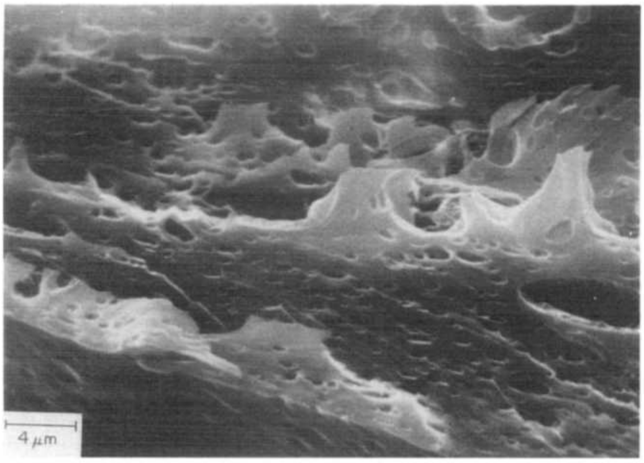

Figure 11 SEM of BTDA+ODA 15% $ATBN_0$ film

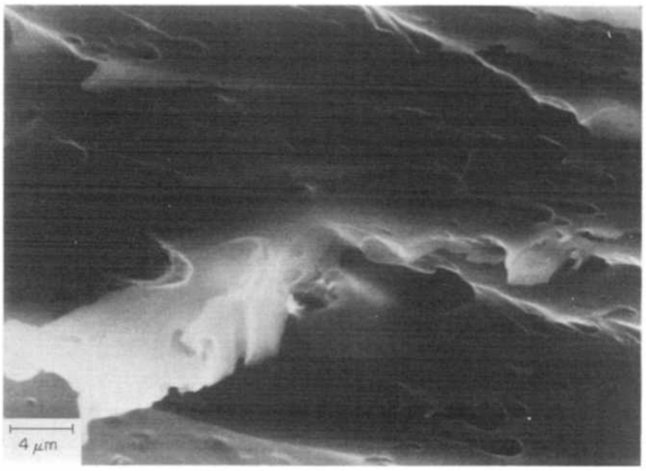

Figure 12 SEM of BTDA+ODA 15% $ATBN_{10}$ film

tear energy appears to have occurred with the film containing 15% of $ATBN_0$. This particular film, however, was almost twice as thick as the others. It is known[14] that tear energies calculated in this fashion vary linearly with film thickness. Data as a function of film thickness are not available in this case, however, so an alternative approach is needed. According to Isherwood and Williams[15], a simple model of the tearing process suggests that tearing force should be proportional to the square of the film thickness, through a proportionality constant which contains the modulus and the work to break. By this measure, one concludes that the film containing $ATBN_0$ is actually less tear-resistant than the control film would be at equal thickness.

When all the data are considered, tear energy shows no clear correlation with tensile properties or morphology of the films. This points to the necessity of fracture characterization if resistance to crack growth is a concern.

CONCLUSIONS

Elastomer-modified polyimide films have been prepared via chemical incorporation of ATBN into BTDA+ODA polyamic acid, and subsequent conversion to polyimide. Optimum cure conditions were found to be a 250°C cure temperature in a N_2 atmosphere. Increasing $ATBN_{18}$ concentration in BTDA+ODA from 0 to 20% produced decreases in thermal stability, tensile properties and density up to 15% $ATBN_{18}$. A 20% $ATBN_{18}$ concentration yielded anomalous room-temperature tensile and density data. Variation of amount of acrylonitrile (18, 10 and 0%) in BTDA+ODA 15% ATBN could not be correlated with tensile data. Films containing $ATBN_{18}$ were found to be more thermally stable than those of lower acrylonitrile content. Densities varied minimally as a result of acrylonitrile variation in BTDA+ODA/ATBN.

Some BTDA+ODA/ATBN films exhibited increases of 17 to 26% in tear resistance relative to BTDA+ODA; the BTDA+ODA/15% $ATBN_{18}$ had the highest tear energy. Tear energies showed no obvious correlation with tensile properties or morphology of BTDA+ODA/ATBN films.

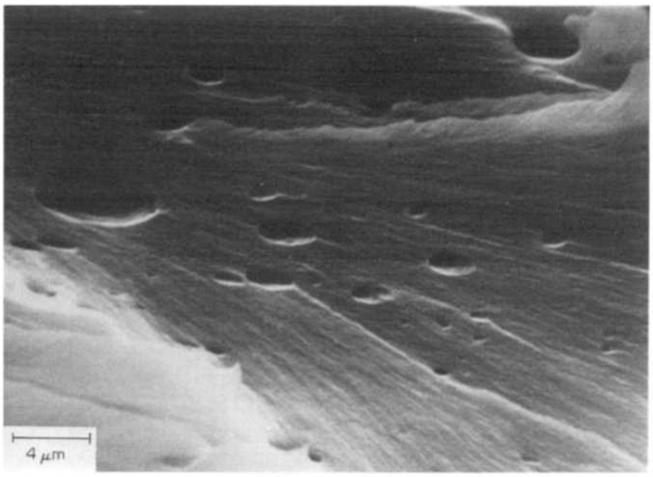

Figure 13 SEM of BTDA+ODA 15% $ATBN_{18}$ film

Table 7 Tearing energies of BTDA+ODA film at 0.51 cm min^{-1} crosshead speed

Elastomer content	T (kJ m^{-2})
0% ATBN	2.05
5% $ATBN_{18}$	2.48
10% $ATBN_{18}$	2.46
15% $ATBN_{18}$	2.59
20% $ATBN_{18}$	1.60
15% $ATBN_0$	3.09[a]
15% $ATBN_{10}$	1.54

[a] Thicker film; see text

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