

Reinforcement of Acrylonitrile Copolymer by Polymer Blending

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Synopsis

Blends of an acrylonitrile copolymer and a reinforcing polymer were formed by polymerization of the second component in a concentrated solution of the first component. The second component, polyureas or polycarbodiimides, precipitated as an intimate dispersion of particulate domains in the liquid medium. Film or fiber formation by coagulation of the solution containing the second component as particulate matter resulted in a distinct two-phase blend. Reinforcement of the acrylonitrile copolymer was evidenced by significant increases in dry and wet moduli above the glass transition temperature of the polyacrylic component. The blends were characterized with dynamic mechanical testing and optical and electron microscopy. The blends exhibited two glass transitions corresponding to those of the individual components. The phase domains were evident over the compositional range examined. The method of blending is illustrative of effective reinforcement by interpenetration of phases in the absence of compatibility of the components at the macromolecular level.

INTRODUCTION

Acrylic fibers are spun from solutions of acrylonitrile copolymers with acrylonitrile content greater than 85%. A major shortcoming of acrylic fibers is their lack of dimensional stability when heated to their glass temperature (T_g) of approximately 80°C in a wet environment. Symptoms of these poor hot-wet properties are a low resistance to deformation, high elongation or creep, and very small restoring force after deformation. The catastrophic drop in storage modulus of acrylic fibers above T_g is associated with a lack of a true crystalline phase to reinforce the noncrystalline phase of the polymer. Although the severe drop in modulus is often tacitly associated with some type of interaction with water, the drop is experimentally found to be very similar in both the wet and dry states above T_g . The predominant influence of water appears to be an approximately 50°C lowering of T_g in the dynamic mechanical spectra. The spectra in the dry and wet states during the glass transition interval are nearly superimposable with an appropriate shift along the temperature axis. However, it should be recognized that water has a major influence upon the "melting transition" temperature of the ordered regions of the acrylic fibers.¹

This research was undertaken to investigate the potential for reinforcing acrylic fibers in their rubbery state (above their glass temperature in water) by the inclusion of particulate matter in the fiber. The polyacrylonitrile copolymers used for fibers are not amenable to melt blending with a reinforcing polymer due to their inherent thermal instability. Blends may be prepared from solution, but here the blend components are severely restricted by the limited number of solvents for acrylic fiber copolymers. Blending of two polymers in a common

solvent also often results in macroheterogeneous phase separation during solvent removal. The synthesis of polyureas and polycarbodiimides with high T_g in a dimethylacetamide (DMAc) solution of acrylic polymer was investigated as a means to achieve dispersion of non-DMAc-soluble reinforcement in the acrylic fiber. The reinforcing effect and blend morphology were examined.

BACKGROUND

In the plastics industry for reinforcement of a rubbery thermoplastic, it has been demonstrated that a fine dispersion of a glassy noncompatible thermoplastic in the rubbery matrix is effective in modulus enhancement without detriment to matrix properties such as elongation.^{2,3} The possibility of enhancing the poor dimensional stability of acrylic fibers in water above 70°C by blending with a rigid polymer has been recognized for some time.⁴ *In situ* polymerization of 2,2-disubstituted propiolactone in dimethylformamide solutions of polyacrylics has been claimed⁵ as a means to achieve a blend fiber of polyacrylic/polyester with improved hot-wet properties. A similar patent⁶ claims the *in situ* polymerization of *p*-aminobenzoyl chloride in dimethylacetamide-lithium chloride solution of polyacrylic to yield a polyacrylic matrix fiber reinforced by poly(1,4-benzamide) particles. The use of polycarbonates in fibrous form in acrylic fiber matrix to improve hot-wet properties has been claimed.⁷

The *in situ* polymerization of diisocyanates in solutions of the polyacrylic was chosen as a model system to evaluate the reinforcing approach.

EXPERIMENTAL

Dynamic Mechanical Measurements

Dynamic mechanical measurements were carried out on a Rheovibron viscoelastometer model DDV-II at 11 Hz. Typical sample dimensions were approximately 0.20 × 5 × 50 mm. The modified sample chamber of Murayama and Armstrong⁸ was utilized for measurements with the sample immersed in water. Samples were heated at 1°C/min between measurements at 5 or 10°C intervals after 5-min equilibration at each measurement temperature.

Characterization of fibers was carried out by similar procedures.

Electron Microscopy

Transmission electron micrographs of films and fibers were taken on a Philips EM-200 transmission electron microscope. Samples were embedded in epoxy resin and sectioned with a Reichert Ultra-Microtome equipped with a diamond knife. Negatives from the electron photomicrographs were used to determine particle sizes and distributions using a Cambridge/Imanco model 720-20 Image Analysis system.

Optical Microscopy

Phase contrast optical microscopy coupled with the Cambridge/Imanco model 720-20 Image Analysis system was used to examine microtomed samples. Certain solutions containing insoluble particulate matter were also examined by

placing a thin smear of the liquid on a slide and allowing the DMAc to evaporate until the residual material was quiescent enough for microscopic examination.

Physical Testing

Single filament tensile testing followed ASTM-2256-24. Tenacity based upon original cross-sectional area and elongation measurements were made at failure. Hot-wet modulus was measured after 1-min immersion in water at 93°C and was calculated as initial modulus.

Inherent viscosities of polyureas were measured for 0.2 g/dl solutions in 95% sulfuric acid at 25°C.

Polyacrylic

A copolymer of acrylonitrile/vinyl acetate (92.7/7.3 wt %) with weight-average molecular weight of 113,000 was used as a substrate.

Polyurea

Reactions were conducted in a 1-liter resin kettle equipped with a mechanical stirrer and blanketed with a nitrogen atmosphere. The stainless steel pitched-blade turbine-type stirrer was operated at 350 rpm. Dried copolymer was dissolved in dry dimethylacetamide by heating to 55°C under a nitrogen blanket. The solution was then cooled to room temperature. In the 10% solids solution, the required quantity of diamine was dissolved, and then the stoichiometric quantity of diisocyanate was added. The medium became opaque within 30 sec after addition of the diisocyanate. A portion of the paste was used to cast films on glass plates with a Gardner knife. The remaining paste was poured into water in a Waring Blender; the polymer was collected by filtration, washed with water, methanol, and acetone, and then dried overnight at 65°C under vacuum. The amounts of diamine and diisocyanate added to the solution were adjusted to give percentages of polyurea based upon total polymer weight and assuming 100% conversion. The neat polyureas were prepared by a similar polymerization procedure, with their concentration in DMAc being 7 to 10 wt %.

Polycarbodiimide

A solution of dried polyacrylic in dry DMAc was prepared. At 55°C the diisocyanate was added. Then 1-ethyl-3-methylphospholine oxide was added to catalyze the polymerization and the medium was stirred for 60 min at 55°C. The paste was cooled to room temperature for film casting.

Film Formation

The paste was spread on glass plates using a Gardner knife. The plates were placed in a 90°C forced air oven for 1 hr. Films were peeled from the plates and clamped in Teflon frames. Films were then given three 1-hr extractions in re-

fluxing methanol (approximately 1:1000 ratio of film to methanol). Films were then washed overnight in running tap water followed by drying at 65°C under vacuum.

The intensity of the 1630 cm^{-1} absorption band in the infrared spectra of the films was monitored as a rough measure of the removal of imbibed DMAc from the films. This band disappeared from the film spectrum after the extraction. The percent residual DMAc in several films was determined by a gas-chromatographic technique for dimethyl sulfoxide solutions of the films with a nitrogen-specific detector. The residual DMAc found in typical films was 4 to 8 wt % after 90°C drying and below 0.015 wt % after extraction.

Fiber Spinning from Polyurea-Containing Dopes

Polymerizations of polyureas in dry DMAc solutions of polyacrylic were carried out in a manner similar to the procedure outlined for films. In a twin-blade helical mixer polyacrylic was dissolved in DMAc at 65°C under nitrogen. The solution was then cooled to 20°C and the diamine was dissolved, followed by addition of the diisocyanate. After 30 min of stirring, the paste was heated to 50°C and then transferred to the spinning pot.

Spinning was from a 100-hole (0.005 in. diam) jet into a 55/45 DMAc/H₂O coagulation bath at 30°C. The fiber was then washed in cold water, drawn in a boiling water cascade, washed with water, and dried on the final godet to give approximately 10 denier per fiber. Filament skeins were shrunk in a steam autoclave to give annealed fibers with elongations to break of greater than 35%.

Reinforcement

Although undesirable side reactions of isocyanates with polar amide solvents such as DMF and DMAc may occur,⁹ it is quite feasible to synthesize reasonably high molecular weight polyureas from aromatic diisocyanates and aliphatic diamines in dry DMAc. For instance, in Table I the characterization data of several polyureas synthesized in DMAc at 10 wt % polymer in the liquid are listed. The use of dry DMAc reaction medium (25 ppm H₂O) suppresses self-condensation of the diisocyanate to yield a polyurea and carbon dioxide.

The TDI-HMD polyurea was found to be sufficiently soluble in DMAc to allow film casting; however, the polymer solution was metastable. None of the other polyureas was soluble at the 10 wt % concentration when formed in DMAc at room temperature.

The polycarbodiimides were synthesized in DMAc using the conventional phospholene oxide catalyst for self-condensation of diisocyanates with evolution of carbon dioxide.¹⁰ The polycarbodiimides precipitated from DMAc and were found to be insoluble and intractable, as expected.¹¹ Yields of the polycarbodiimides were greater than 95%. The glass temperatures of the polycarbodiimides derived from 2,4-diisocyanatotoluene (TDI) and 4,4'-diisocyanatodiphenylmethane (MDI) should be around 200°C based upon the mechanical measurements reported by Alberino et al.¹¹ for related structures.

A reinforcing effect was found for films cast from the DMAc dopes of polyacrylic containing various concentrations of *in situ* polymerized polyureas. The

TABLE I
Characterization of Polyureas Synthesized in DMAc

Abbreviation	Composition	Polymer yield, %	η_{inh}	$T_g, ^\circ C$	$T_m, ^\circ C$
MDI-HMD Polyurea		94	0.68	~200	266
TDI-HMD Polyurea		97	1.34	210	amorphous
HMI-PIP Polyurea		96	1.40	~200	270

storage modulus (E') data for this series of films are summarized in Tables II and III. The modulus values of the separate components of the blend are similar, below T_g of the acrylic copolymer. At temperatures above T_g of the acrylic ($\sim 120^\circ\text{C}$ dry and 80°C wet), the polyurea is still glassy and exhibits a modulus of 1.0×10^9 Pa. Consequently, no reinforcing effect is apparent for the blends until the T_g of the acrylic component is exceeded. At 150°C dry and 93°C wet, the blend films exhibit modulus values considerably higher than those of the softer component. This effect is shown in Figure 1, where the dynamic mechanical spectra of the components and blends are compared. The polyurea remains glassy to a temperature of 200°C , exhibiting a damping ($\tan \delta$) maximum between 200 and 220°C . The acrylic exhibits its typical softening around 100°C , with a damping maximum around 110 to 130°C . The blend shows considerable stiffening compared to polyacrylic above 110°C , as measured by the storage modulus, but the damping maximum was not shifted along the temperature axis. The loss modulus (E'') data of the blends also exhibit the two T_g values corresponding to those of individual components.

It should be noted that the characteristic degradative cyclization of side chains of the acrylonitrile copolymer may affect the dynamic mechanical spectra at temperatures in excess of 180°C .

Tables II and III also present data that show the reinforcing effect to be present in water. The precipitous decline in storage modulus (1.5 decade decrease) over a 30 to 40°C interval above T_g , which is characteristic of acrylonitrile copolymers, is shifted from an onset at 100°C when dry to 60°C when wet. The general features of the storage modulus curve are not altered in water relative to a dry

TABLE II
Storage Modulus Ratio Relative to Polyacrylic for Films Reinforced with TDI-HMD Polyurea

Polyurea, wt %	Dry (blend modulus/acrylic modulus)				Wet (blend modulus/acrylic modulus)			
	30°C	93°C	120°C	150°C	30°C	60°C	80°C	93°C
19.2	1.46	1.93	4.72	6.59	0.67	0.67	1.20	2.41
28.4	0.61	1.09	3.45	5.45	1.53	1.64	1.93	3.91
35.7	1.01	1.26	4.45	7.50	1.13	1.00	1.83	3.45
44.2	1.07	1.60	4.18	6.13	1.53	1.73	3.33	6.89
50.0	a	a	a	a	a	a	a	a
100.0	0.68	1.24	7.72	19.31	1.27	1.64	5.67	14.94

^a Film was so brittle that mechanical integrity could not be maintained for Vibron measurement.

TABLE III
Storage Modulus Ratio Relative to Polyacrylic for Films Reinforced with MDI-HMD Polyurea

Polyurea, wt %	Dry (blend modulus/acrylic modulus)				Wet (blend modulus/acrylic modulus)			
	30°C	93°C	120°C	150°C	30°C	60°C	80°C	93°C
10.7	1.16	1.14	1.88	2.67	0.73	0.91	0.90	1.61
16.7	1.05	0.93	1.17	2.50	1.47	1.18	1.60	2.30
21.8	1.05	1.07	2.50	2.83	0.63	0.73	0.87	1.84
38.0	0.42	0.43	0.83	1.83	0.27	0.22	0.63	1.26
50.0	0.37	0.43	1.46	3.00	0.47	0.36	0.47	0.75

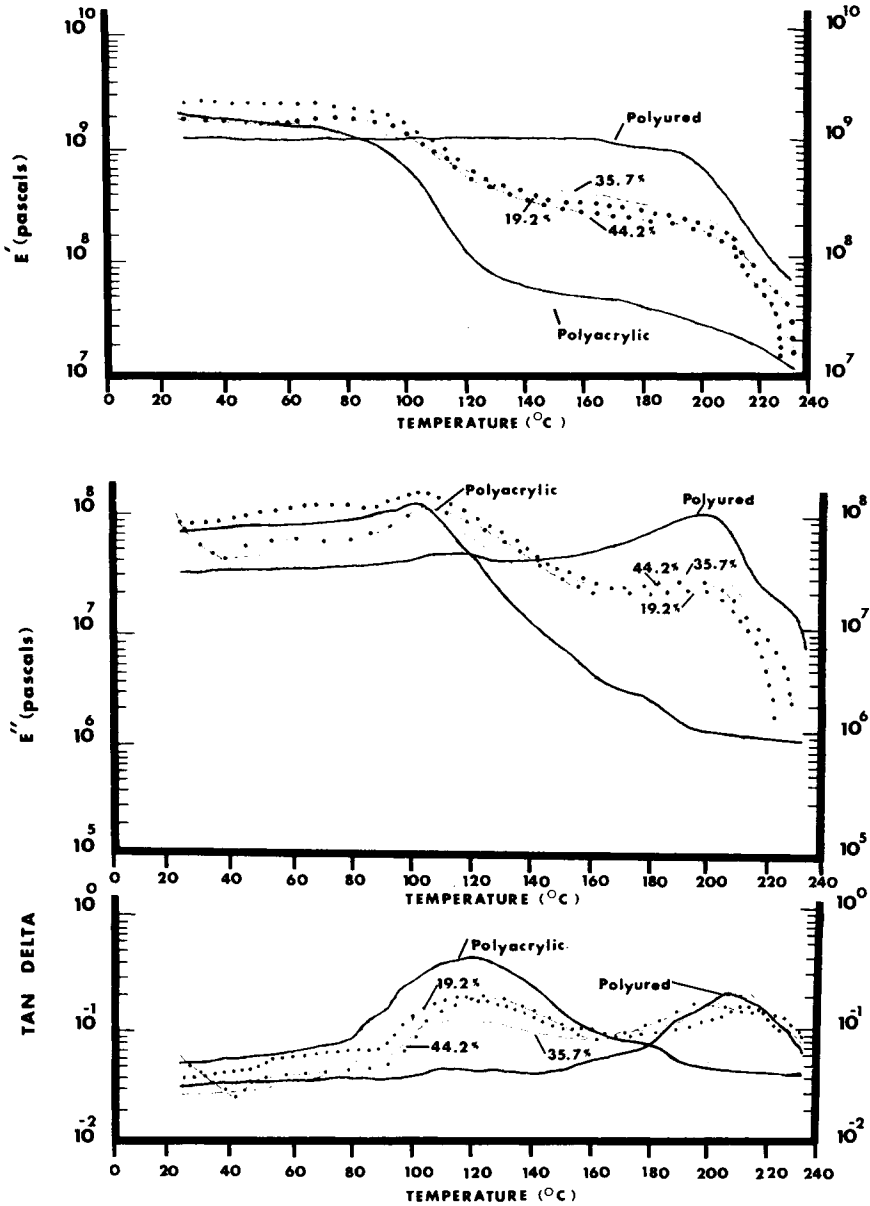


Fig. 1. Comparison of dry dynamic mechanical properties of blends containing TDI-HMD polyurea with spectra of the components.

medium, only shifted along the temperature axis. The presence of the polyurea with its wet T_g above 100°C and a storage modulus of 1×10^9 Pa up to 100°C results in significant reinforcement of the acrylic component between 70 and 100°C when wet. Again the damping peak at 70 to 80°C for the blend is not significantly shifted relative to the peak for the acrylic component. Figure 2 compares the dynamic mechanical properties in water of a blend with that of the acrylic component.

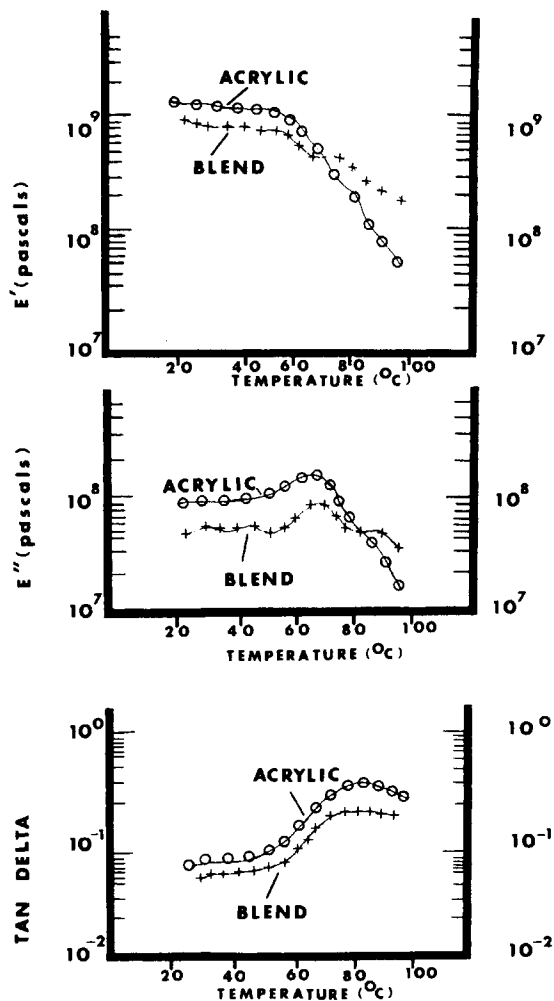


Fig. 2. Comparison of dynamic mechanical properties in water of polyacrylic component with blend containing 19.2% TDI-HMD polyurea.

To confirm the presence of the reinforcing polymer in the films, infrared spectra were compared with those of the pure components, and the expected characteristic absorption bands of the components were found in the blend films. The acrylic component of the blend was extracted in dimethylformamide at room temperature and the residual polyurea collected by centrifuging. The residual polyurea was thoroughly washed and dried. Recovery exceeded 90 wt % of the calculated quantity of polyurea in the blends. The recovered polyureas had inherent viscosities similar to those of the same polyureas synthesized in DMAc without polyacrylic being present.

In Tables II and III, there are indications that the storage moduli of the blends reach a maximum as the percentages of polyurea in the films increase, and then the moduli decrease as 50% polyurea is approached. For films containing the

MDI-HMD polyurea, the storage moduli both below and above T_g of the acrylic component exhibit a salient decrease for the two higher concentrations of polyurea. The damping and loss moduli are also significantly lower than those of the other blends with lower polyurea concentrations.

The reinforcing effects in films of several polyureas and polycarbodiimides at comparable weight percentages are presented in Table IV. Clearly, the polyureas derived from 2,4-diisocyanatotoluene (TDI) and hexamethylenediamine (HMD) or ethylenediamine (ED) are most effective along with the polycarbodiimide derived from this diisocyanate. The glass transition temperature of the TDI-ED polyurea has been reported as 190°C.¹² Considerable reinforcement was found with all of the structures except entry 4. The partially crystalline nature of entries 3, 4, and possibly 5 may account for their diminished effect. It might be speculated that the polymers with structural characteristics leading to crystallinity would phase segregate in a blend to a greater extent and have less interphase adhesion than amorphous polyureas and polycarbodiimides.

A structural modification of the TDI-HMD polyurea was investigated as a means to achieve greater reinforcement. Crosslinking of the polyurea by substitution of a trifunctional polyisocyanate for a portion of the 2,4-diisocyanatotoluene was tested. A polyurea with a ratio of triisocyanate equivalent to total isocyanate equivalents of 0.1 was prepared in DMAc and was found to be insoluble in 95% H₂SO₄. When this crosslinked polyurea was prepared in an acrylic solution, no enhancement of the reinforcing effect was found. Domain size for the crosslinked polyurea was similar to that of the uncrosslinked structure.

The reinforcing effect of the polyureas was translatable to fibers. Spinning solutions containing precipitated polyurea were very pasty and opaque. A standard ball fall technique of determining spinning solution viscosity was not applicable since the ball remained indefinitely on the upper surface of the pasty mass. However, spinning of the paste was accomplished under conditions used for the polyacrylic control fiber.

Tensile properties of fibers containing the polyureas are presented in Table V. Comparison of entry 1 with 2 and 3 indicates that fibers with tenacity, elongation, and knot strength equivalent to those of the unmodified acrylic were obtained under conventional spinning conditions. Yet the polyurea-containing fibers exhibited a threefold increase in hot-wet modulus with 15 to 20 wt % reinforcement. Unlike crosslinking reactions to increase the resistance of acrylic fibers to deformation above T_g , the blend reinforcement does not embrittle the fibers, as evidenced by the elongation values and excellent retention of tenacity in the knot test.

The dynamic mechanical properties of an unmodified acrylic fiber and a fiber with 20 wt % reinforcement are compared in Figure 3. The expected reinforcing effect above T_g was evidenced in the storage moduli curves both wet and dry. Yet the damping peak associated with the onset of segmental mobility of the matrix is not greatly altered by the presence of the polyurea.

Entry 4 in Table V illustrates that the MDI-HMD polyurea is considerably less effective than the TDI-HMD polyurea, just as was found in films.

TABLE IV
Comparison of Storage Modulus Increase for Various Reinforcing Polymer Structures in Films

Entry no.	Abbreviation	Structure	Wt % in film	Blend modulus/acrylic modulus	
				93°C Wet	150°C Dry
1	TDI-HMD Polyurea		19.2 28.4	2.4 3.9	4.1 4.5
2	TDI-ED Polyurea		28.4	2.8	4.5
3	MDI-HMD Polyurea		16.7 21.8	1.8 1.7	2.8 2.5
4	HMI-PIP Polyurea		16.7	1.0	0.9
5	MDI Polycarbodiimide		16.7	1.6	1.7
6	TDI Polycarbodiimide		16.7	2.1	1.7

TABLE V
Tensile Properties of Acrylic Fibers Containing Reinforcement Synthesized in the Solution

Entry no.	Reinforcement	Wt % total solids in fiber in solution	Wt % total solids in fiber in solution	Cas- cade stretch	As spun					Annealed		
					Ultimate tenacity, Pa	Ultimate elongation, %	% Relative tenacity (knot test)	Hot-wet modulus, Pa, 93°C H ₂ O	Ultimate tenacity, Pa	Ultimate elongation, %	% Relative tenacity (knot test)	Hot-wet modulus, Pa, 93°C H ₂ O
1	none	-	25	6.0	3.5×10^8	16.0	22.6	1.8×10^8	2.4×10^8	44.0	95.5	0.5×10^8
2	TDI-HMD Polyurea	20	21	6.0	3.5×10^8	17.7	13.9	2.4×10^8	1.7×10^8	68.4	96.7	1.7×10^8
3	TDI-HMD Polyurea	20	25	6.0	3.5×10^8	17.9	12.7	2.6×10^8	2.3×10^8	64.0	95.9	1.3×10^8
4	MDI-HMD Polyurea	15	21	5.0	2.6×10^8	16.5	10.6	2.0×10^8	1.9×10^8	37.7	63.7	0.5×10^8

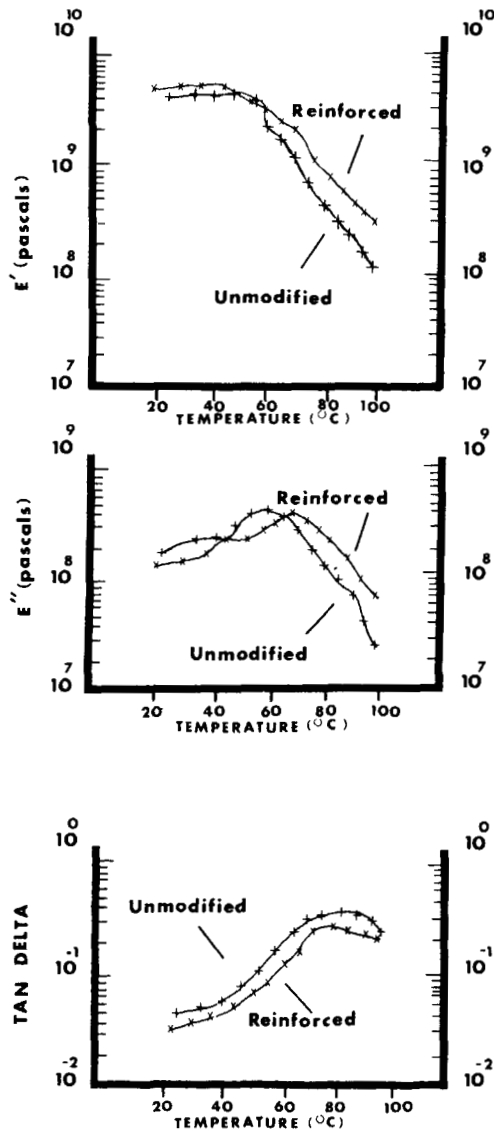


Fig. 3. Comparison in water of unmodified and reinforced fibers which were annealed.

Domain Morphology

Optical phase contrast microscopy was utilized to determine domain size for microtomed 3- to 5- μm sections of films and fibers in conjunction with the Cambridge/Imanco Image Analysis system. The transmission electron microscope was used for a more detailed examination of ultramicrotomed 0.06- to 0.09- μm sections, also utilizing the image analysis system for domain size characterization.

The electron micrographs have the appearance of polyurea domains in an acrylic matrix. The sizes of the polyurea domains are compared in Table VI for varying concentrations of two polyureas. Both the optical and electron-microscopic measurements indicate that the average longest dimension was between

TABLE VI
Mean Size of Domains in Films

Reinforcement	Wt % reinforcement in film	Mean longest dimension, μm	Transmission electron microscopy		Phase contrast optical microscopy mean longest dimension, μm
			Mean length/breadth ratio	Magnification	
MDI-HMD Polyurea ↓ TDI-HMD Polyurea	10.7	1.14	3.7	1656	1.3
	16.7	1.01	3.6	1636	2.0
	21.8	0.89	3.2	1656	2.0
	38.0	0.43	2.8	2700	—
	50.0	1.43	3.4	1656	—
TDI-HMD Polyurea ↓	19.2	1.81	2.7	1656	3.5
	28.4	1.97	3.7	1656	3.0
	35.7	1.45	3.5	1656	3.0
	44.2	1.78	3.2	1656	—
	50.0	2.40	3.7	1656	—

0.5 and 4 μm . The two techniques probably differ in sensitivity of the detection means to resolve phase domains.

In a typical distribution from the electron micrographs, the minimum value of longest dimension was 0.3 μm and the maximum 4 μm , with the mean value being 1 μm .

In Figures 4 and 5, electron micrographs of films with varying concentrations of polyureas are compared. The MDI-HMD polyurea appears to be present as definite particulate domains in an acrylic matrix. As the concentration of the polyurea approaches 50%, the continuous character of the matrix appears to decrease, which corresponds to the loss of the reinforcing effect at 50% polyurea. There is also some evidence for separation at the interphase between polyurea particles and matrix, which may be an indication of poor adhesion of the two phases. The contrast between the polyurea phase and the acrylic phase is quite distinct. However, for the TDI-HMD polyurea, the contrast is much less distinct. This lack of contrast might be due to similarities in electron densities between the two phases or to partial interpenetration of the two phases. The finding that TDI-HMD domains are less well defined than those of MDI-HMD polyurea may be related to the more effective reinforcement gained with the former polyurea. Perhaps there is partial interpenetration of domains for the TDI-HMD/acrylic blends, that is, inclusions of one phase in the domains of the other phase. The existence of two mechanical dispersions corresponding to the glass transitions of the two components indicates no interpenetration at the macromolecular level.

The phase definition in reinforced fibers containing these two polyureas is compared in Figure 6. In cross sections perpendicular to the fiber axis, both polyureas appear to be particulate, with some separation at the interphase for

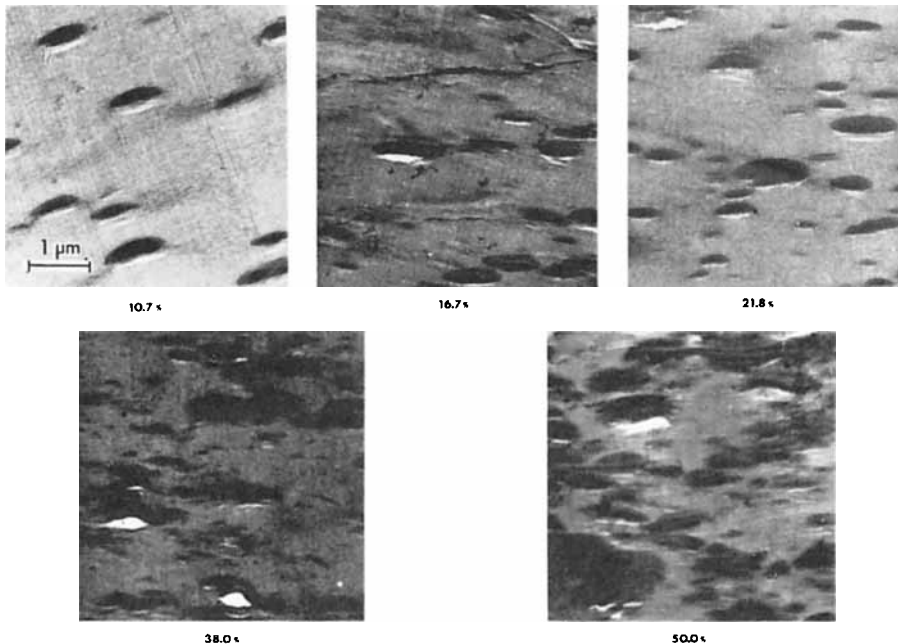


Fig. 4. Electron micrographs of films containing MDI-HMD polyurea.

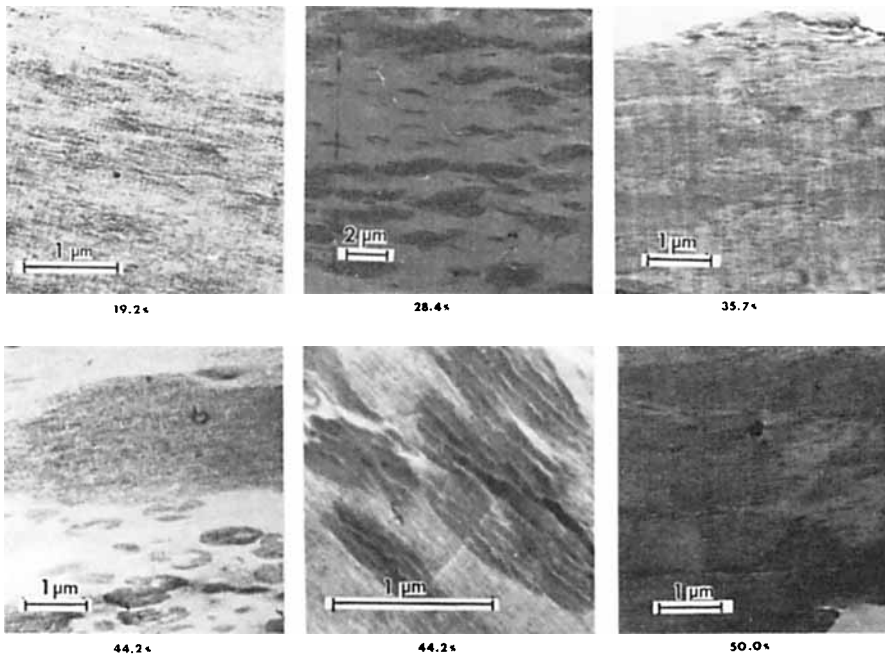


Fig. 5. Electron micrographs of films containing TDI-HMD polyurea.

the MDI-HMD polyurea but not for the TDI-HMD polyurea. In the lateral sections, the MDI-HMD polyurea appears to be dispersed as particles, with some separation at the interphase. The TDI-HMD polyurea does not appear as distinct domains contrasted against the matrix in the lateral section. However, phase contrast optical microscopy indicated that for the TDI-HMD polyurea there were definite micron-size domains in the fiber. Again, one is tempted to draw a correlation between an apparent adhesion and interpenetration of the TDI-HMD polyurea domains with the matrix and their effectiveness as a reinforcement.

Both optical and electron microscopy indicated that the mean particle size for the polyureas in fibers was smaller than in the films. In fibers, a typical mean longest dimension of the polyurea features would be $0.3 \mu\text{m}$, versus $1 \mu\text{m}$ in films, as determined from electron micrographs. The agitation achieved in the mixer used for spinning solution preparation versus the laboratory stirrer used for film preparation probably accounts for the difference in feature size. Control of domain size through the *in situ* polymerization and precipitation processes is a variable which was not investigated. Variables such as solution viscosity, agitation, temperature, and addition procedure might well affect the domain size and distribution.

The polyacrylic solutions containing the second component as precipitated polymer were also examined by phase contrast optical microscopy. After room-temperature evaporation of sufficient solvent for the smear to become quiescent, both mean particle size and distribution were similar to those found for the dried film cast from the same paste.

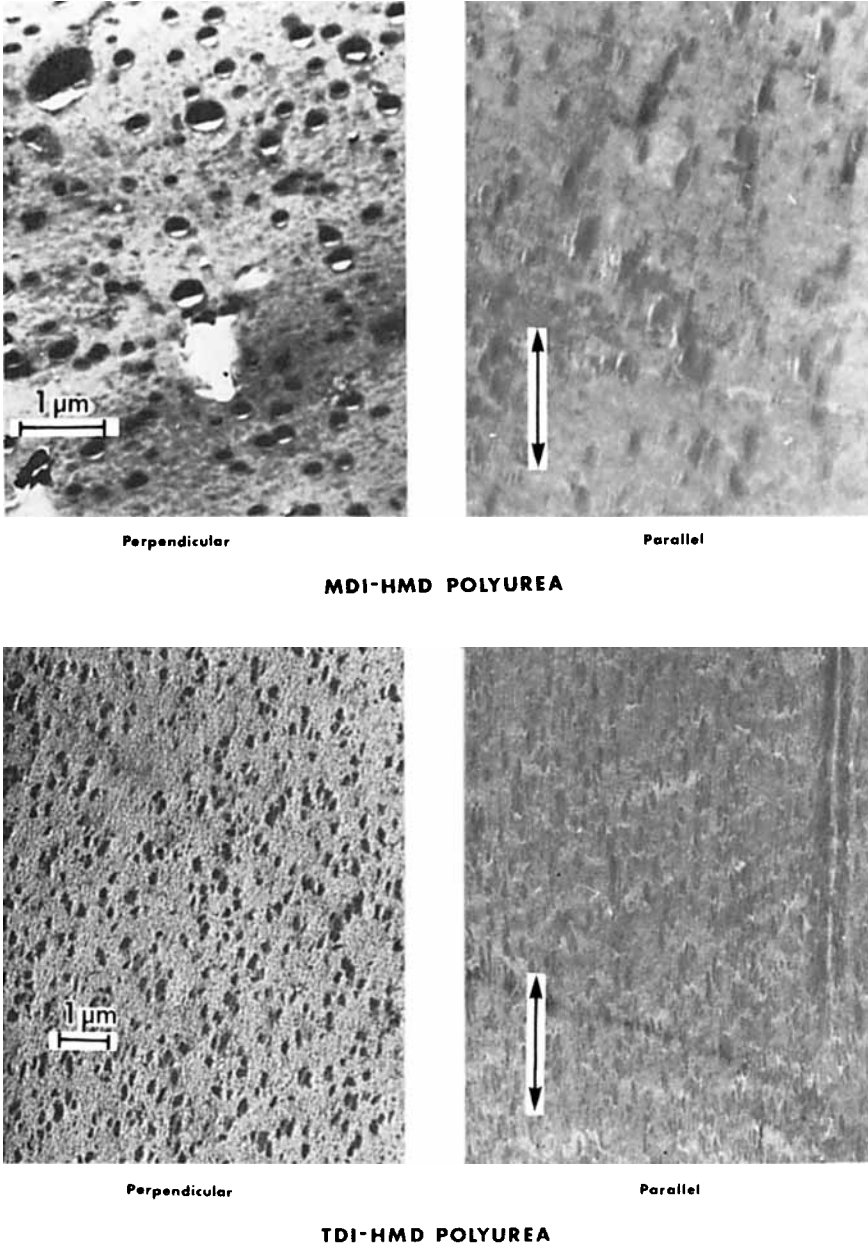


Fig. 6. Electron micrographs of fibers containing 15% polyurea sectioned relative to fiber axis.

DISCUSSION

A favorite tool for classifying polymer blend behavior is to compare moduli-versus-composition plots against curves calculated from analytical relations based upon models. In many models a discrete particulate phase dispersed in a continuous matrix is assumed. Others assume an elementary series or parallel arrangement of phases. More elaborate models assume that a two-phase material can be treated as mixtures of series and parallel elements. Mathematical rela-

tionships have also been proposed which fit fairly well the behavior of blends where both phases are continuous. Excellent discussions of the applicability and interpretation of these models have recently appeared.^{3,13-16} For simplicity, the parallel arrangement of discrete phases provides an absolute *upper* limit on the dynamic complex modulus of the blend:

$$E^* = E_s^* + \phi(E_H^* - E_s^*)$$

where E^* is the blend modulus; E_s^* and E_H^* are the moduli of the soft and hard phases, respectively; and ϕ is the volume fraction of the hard phase. A series arrangement of discrete phases gives an absolute *lower* limit on the blend modulus:

$$E^* = \left[\frac{1}{E_s^*} + \left(\frac{1}{E_H^*} - \frac{1}{E_s^*} \right) \phi \right]^{-1}$$

The expressions for E^* can be separated into real and imaginary parts to give explicit expressions for E' and E'' . These bounds are based on the assumption that properties of blend components are the same in the blend as in bulk. The upper bound is an isostrain arrangement, while the lower is an isostress arrangement. The parallel upper bound corresponds closely to the model where the stiffer component is continuous with soft inclusions, while the series lower bound corresponds to the model where the softer component is continuous with hard dispersions.

The storage moduli of films at 150°C versus composition are shown in Figure 7. The upper and lower bounds were calculated using the moduli of the acrylic film and the TDI-HMD polyurea film. Weight fractions were substituted for volume fraction in the equations. The modulus of the pure MDI-HMD polyurea

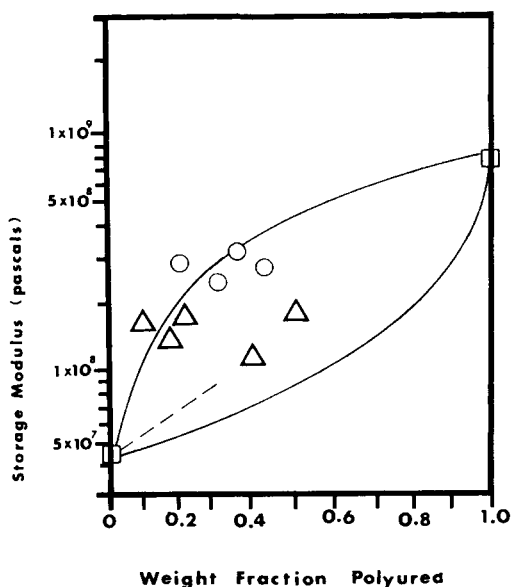


Fig. 7. Storage moduli of dry films at 150°C vs. weight fraction of polyurea. Upper and lower curves were calculated for parallel and series bounds, respectively. Dashed line was calculated for a model of discrete polyurea phase of spheres in an acrylic matrix: (□) individual components; (○) TDI-HMD polyurea; (△) MDI-HMD polyurea.

was not available due to the polymer's insolubility. Attempts to press this polyurea into a film with heat were unsuccessful. However, the modulus of this polyurea would not be expected to differ greatly from the 0.9×10^9 Pa value of the TDI-HMD polyurea. Literature values¹¹ for the moduli of aromatic polycarbodiimides similar to those prepared in this study indicate that the upper and lower bounds shown in Figure 7 might also be used for these reinforcements. The dashed line shown in Figure 7 is based upon the equation developed by Locke and Paul¹⁷ for a discrete phase of spheres in a matrix.

The moduli values of the TDI-HMD polyurea-reinforced blends are clearly closer to those of the upper bound. If a model of simple inclusions is assumed, the closeness of the moduli to the upper bound indicates a hard continuous phase. The constancy of the moduli with increasing hard-phase volume fraction might be treated by a model with composite inclusions in a hard continuous phase. The loss tangent and storage modulus-versus-temperature curves of Figure 1 are also somewhat consistent with the hard continuous phase with soft inclusion model as shown for an idealized case by Dickie.¹⁶ However, microscopic characterization (Figs. 4, 5, and 6) of these blends seems more indicative of an acrylic matrix with discrete dispersed particulate domains of polyurea, especially for the MDI-HMD polyurea. In the micrographs, concentrations of polyurea greater than 35 wt % appear to correspond to increased continuous character for the darker phase, presumably polyurea. Yet, above this concentration, storage moduli compared against upper and lower bounds indicate decreasing continuity of the hard phase.

The regions perceived as polyacrylic matrix and polyurea dispersed domains in the micrographs may also have significant undetected phase boundaries of mixed composition. These interfacial regions would correspond to greater interpenetration of phases than is implied from the micrographs. Both matrix and dispersed phase mechanical properties might be considerably altered in such a blend from those in bulk. The application of models to such systems becomes inappropriate.

A domain morphology with both phases exhibiting continuous character would also result in blend moduli approaching the upper bound.³ We are attempting to microscopically examine domain connectivity through selective dissolution of components. The magnitude of the reinforcement of storage modulus shown in Figure 7 is consistent with degree of dual phase continuity achieved in interpenetrating polymer networks.¹⁸ Such connectivity of the polyurea domains appears inconsistent with the method of blend preparation and other evidence, i.e., Figures 4, 5, and 6, and the discussion of tensile strength above T_g of the polyacrylic component that follows.

Morton et al.^{19,20} showed that for the elastomer-polystyrene latex blends there was no reinforcing effect in tensile strength at break when both phases were glassy. However, when the elastomeric matrix was above T_g , tensile strengths were increased by a factor of 10 by adding 25% polystyrene. Morton et al.^{19,20} concluded that the reinforcement acted by increasing matrix viscosity. The ultimate mechanical behavior of interpenetrating polymer networks of rubbery and plastic homopolymers has been studied.¹⁸ For a rubbery matrix above its T_g interpenetrated by a less continuous plastic phase, there is an increase in both stress-to-break and ultimate elongation.

Tensile strength of the polyacrylic-polyurea fibers was tested above T_g of the

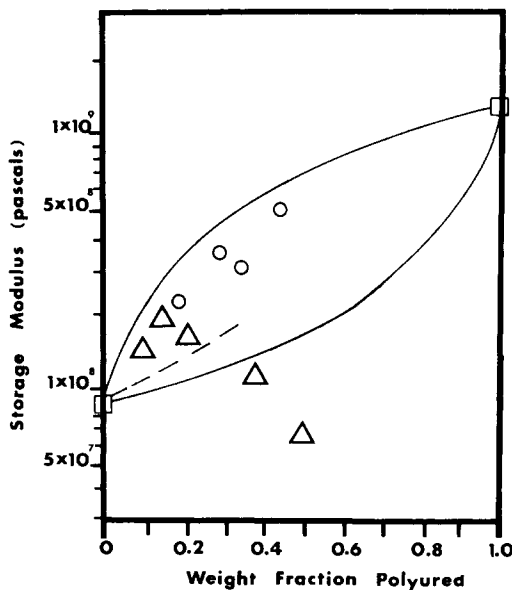


Fig. 8. Storage moduli of wet films at 93°C vs. weight fraction of polyurea. Upper and lower curves were calculated for parallel and series bounds, respectively. Dashed line was calculated for a model of discrete polyurea phase of spheres in an acrylic matrix: (□) individual components; (○) TDI-HMD polyurea; (Δ) MDI-HMD polyurea.

acrylic to see if a reinforcement in tenacity appeared. Results from a tensile testing at 150°C dry and 93°C wet are shown in Table VII. The tabulation shows that there was no increase in tenacity but an appreciable increase in initial modulus. The difference in moduli of the blend versus the control fiber was well within the limits of being statistically significant at the 95% confidence interval. The data are consistent with a reinforcing mode where at large strains the properties of the polyacrylic dominate the mechanical behavior of the blend.

It would appear likely that the reinforcing effect exhibited by an increase in modulus parallel to the fiber axis would also be observed in other directions. Electron micrographs indicate that there is no marked orientation or fibrillation of the polyurea phase in the fiber axis direction. The globular nature of the polyurea domains with their excellent interpenetration with the fiber matrix should result in reinforcement in all directions. The transmission electron micrographs of fiber reinforced with 20% polyurea were examined for sections parallel and perpendicular to the fiber axis. The mean longest dimension and length-to-breadth ratio were 0.38 μm and 2.6, respectively, in both directions.

A comparison of the reinforcing effect against upper and lower bounds in the wet state at 93°C is presented in Figure 8. The TDI-HMD polyurea again approaches the upper bound. However, the MDI-HMD polyurea exhibits a catastrophic decline in reinforcing effect beyond 18 wt % concentration. In the dry state shown in Figure 7, the reinforcing effect of this polyurea appears to reach a plateau at 20 wt % but does not fall below the lower bound. In water, the moduli fall well below the lower bound, probably indicative of a loss in mechanical integrity of the blend films in water. The electron micrographs for this blend shown in Figure 4 indicate a tendency toward interphase separation. Such separation is not evident for the TDI-HMD polyurea shown in Figure 5.

TABLE VII
Comparison of Tensile Properties Above Glass Transition of the Polyacrylic Component

Test conditions	Reinforcement	Ultimate tanacity, Pa	Ultimate elongation, %	Initial modulus, Pa	% Relative tenacity retention in knot test
150°C Dry	none/as spun	1.2×10^8	100	3.6×10^8	112
	20% TDI-HMD/as spun	1.2×10^8	90	5.9×10^8	83
150°C Dry	none/annealed	0.5×10^8	231	1.1×10^8	99
	20% TDI-HMD/annealed	0.5×10^8	218	3.3×10^8	99
93°C Wet	none/as spun	0.7×10^8	95	2.2×10^8	98
	20% TDI-HMD/as spun	0.7×10^8	99	2.5×10^8	96
93°C Wet	none/annealed	0.5×10^8	226	0.7×10^8	96
	20% TDI-HMD/annealed	0.5×10^8	177	1.7×10^8	96

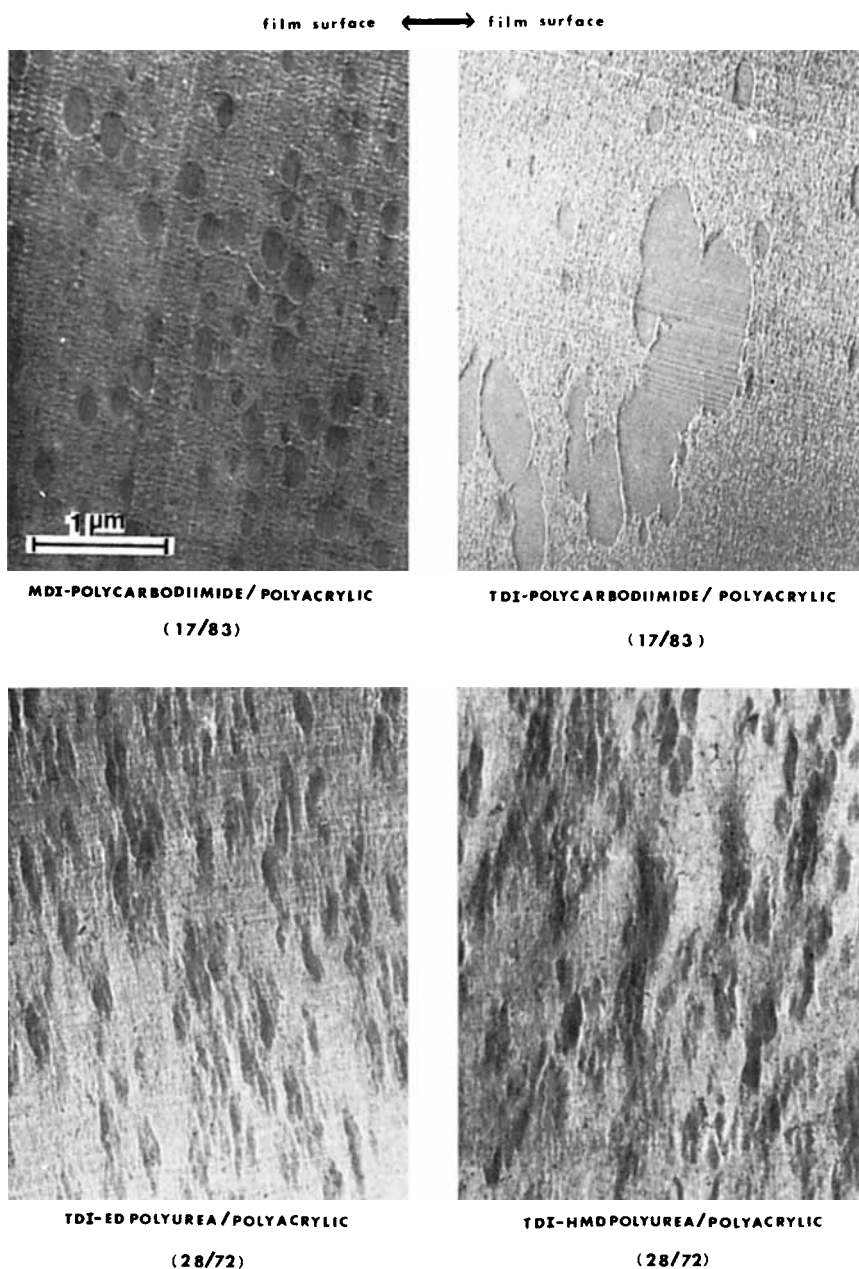


Fig. 9. Electron micrographs of blend films exhibiting various morphologies.

A variety of domain morphologies was observed in the electron photomicrographs of various films and fibers. Figure 9 illustrates some of these features. The polycarbodiimides appear to be present as very discrete elliptical particles in the matrix. The MDI-polycarbodiimide appears as nearly monodisperse elliptical particles, while the TDI-polycarbodiimide has a somewhat similar feature with the particles being coalesced or agglomerated in some cases. The agglomeration may be related to the amorphous and more DMAc-soluble nature

of the TDI structure. The contrast between the TDI-derived polyureas and the acrylic phase is much less distinct than for the polycarbodiimides. The polyureas are much less distinct as geometric features. When sections perpendicular to the film surfaces were taken at 90°, the general appearances of the features were the same, indicating a globular character.

The formation of a blend by simultaneous polymerization-precipitation of the second component in a concentrated solution of the first component has certain features analogous to mixing²¹ two latex polymers. Removal of the liquid can result in a fine particulate dispersion of the second component with the first component. The size and distribution of phase domains can probably be controlled by the *in situ* polymerization process for the second component and the coagulation process for the first component.

The particle size and distribution of the second component appear to be largely determined at the time of polymerization, and little tendency toward agglomeration has been observed. There is also an opportunity for physical entrapment of one phase in the other during the precipitation of the second component. The liquid media might enhance intermixing by plasticizing and swelling the precipitated second component and the first component during its coagulation. Unlike solution blending, there is not a high mobility of both components during solvent removal, resulting in macroheterogeneous phase separation. The necessity of a mutual solvent for solution blending is also avoided. The existence of a suitable polymerization process for the second insoluble component in the solution of the first is needed.

CONCLUSIONS

1. *In situ* polymerization of diisocyanates and diamines in DMA solutions of acrylonitrile copolymer used for conventional wet spinning resulted in polymer blends exhibiting reinforcement and interpenetration of phases.

2. The damping peaks of the polyacrylic and the polyurea components of the blend coincide with the damping peaks of the pure components. A distinct two-phase blend was indicated by dynamic mechanical testing.

3. Microscopic characterization indicated a two-phase morphology with interpenetration of phases. The polyurea domains had mean longest dimension, of the order of 1–3 μm .

4. The magnitude of the reinforcement seems inconsistent with other evidence which indicates a dispersed polyurea phase in an acrylic matrix.

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