Polymer, 1991, Vol. 32, 88–94

A novel heat-resistant blend produced by compositional quenching: a thermoplastic polyimide impact-modified with a fluoroelastomer

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(Received 22 September 1989; revised 16 January 1990; accepted 19 January 1990)

A novel high-temperature blend consisting of a microdispersion of the fluoroelastomer Viton A in an Ultem poly(ether imide) matrix has been produced through the process of compositional quenching. Submicrometre spherical particles of the elastomer were formed within the poly(ether imide) matrix through the process. It has been found that the addition of Viton to Ultem significantly improves impact strength with little sacrifice in tensile properties and thermal stability. This improvement in impact strength becomes even more dramatic at elevated temperatures. These impact strength improvements are attributed to the rubber particle's ability to activate shear yielding deformation in a larger volume of the matrix material near the tip of a propagating crack. This deformation absorbs energy during fracture and results in higher impact strengths. Blends of Ultem and Viton produced by extrusion and precipitation processes were found to have problems that were not observed in any of the compositionally quenched materials.

(Keywords: poly(imide ether); fluoroelastomer; impact-modified; compositional quenching)

INTRODUCTION

The impact modification of polymers is possible through incorporation of rubbery phase domains into an otherwise brittle polymer matrix. High-impact polystyrene (HIPS), acrylonitrile–butadiene–styrene (ABS) and modified epoxies are well known and important materials that employ this technique. The size of the rubber phase domains in many cases determines the degree of toughening that occurs in a particular system. Two-phase rubber/polymer blends have been produced by a number of methods. These methods include mechanical blending, precipitation polymerization, emulsion polymerization and block copolymerization. These existing processes have limitations and cannot always be used to produce the desired microdispersion[1]. A process, called compositional quenching, has been developed in which a blend of a finely dispersed rubbery phase within a continuous polymer phase can be created by rapid removal of the solvent from a single-phase polymer solution. As the solvent is being removed, phase separation occurs by spinodal decomposition[1]. The size of the rubber phase domains is, in part, a function of the rate of solvent removal. High rates of solvent removal produce very small particles[2,3].

In this work, we explore using compositional quenching in the rubber modification of a high-temperature polymer, a poly(ether imide) known as Ultem 1000. Polymers of this type are particularly interesting for military, electronic and automotive applications where thermal stability is important. However, most heat-resistant polymers are usually quite brittle. This brittleness is often due to the stiff polymer backbone that also imparts the high thermal stability. It is difficult to alter the polymer backbone to add toughness without adversely affecting thermal stability. The addition of a thermally stable elastomer as an impact modifier is one means to improve the toughness of high-temperature polymers without greatly sacrificing heat resistance.

The equipment used for compositional quenching is schematically shown in *Figure 1*. The single-phase polymer solution is first pumped through a heat exchanger in order to accept heat, which will ultimately be used to vaporize the solvent. The polymer solution is typically heated to 200–300°C. In order to prevent the solvent from boiling within the heat exchanger and in the lines before the flash chamber, the heated solution is kept under relatively high pressure, typically over 500 psi. This heated, pressurized solution is then flashed across a valve into an evacuated chamber. Most of the solvent rapidly vaporizes and exits through the top of the flash chamber, leaving behind a two-phase polymer blend. The solvent vapours can be condensed, collected and recycled. The polymer blend is collected at the bottom of the flash chamber for further processing. The polymer product often contains large amounts of solvent, typically about 50% by weight, so that further devolatilization is needed. Despite the residual solvent, the mixture collected in the flash chamber has a relatively high viscosity. This high viscosity lowers molecular and Brownian diffusion and prevents agglomeration or coarsening of the rubber phase. The product is a viscosity-stabilized suspension of rubber particles in a continuous polymer matrix that is sufficiently stable to survive subsequent processing.

Polyimides, characterized by their five-membered nitrogen-containing ring, are particularly known for their

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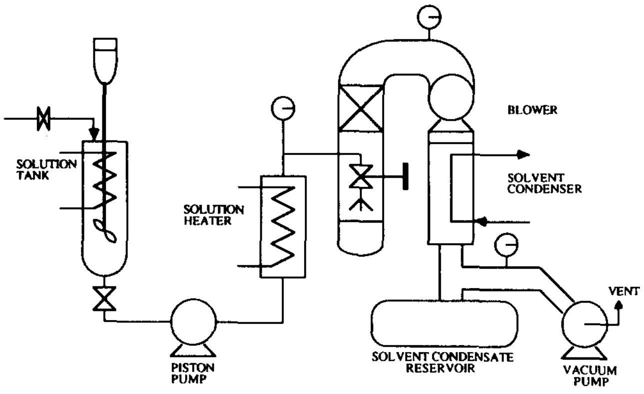

Figure 1 Schematic diagram of compositional quenching apparatus

thermal stability. Polyimides come in the form of both thermoset and thermoplastic polymers. One polyimide that includes ether linkages to provide its thermoplastic nature is sold by the General Electric Co. under the tradename of Ultem. Ultem is commonly used for electrical components and in aircraft. Ultem 1000, a high-viscosity no-additives grade, was used in this study. Viton A, a fluorelastomer produced by DuPont, was chosen as the modifying agent due to its thermal stability. Viton can withstand temperatures in excess of 200°C without significant degradation. Dimethyl formamide (DMF) was found to dissolve both Ultem and Viton as required for the compositional quenching process. No block copolymers or surface-active agents were employed in any of the experiments that follow.

EXPERIMENTAL

The single-phase polymer solution required as the feed for the compositional quenching process consisted of 2.5% by weight of the combined polymers in dimethyl formamide. Blends containing 5, 10 and 15% by weight of Viton A in Ultem 1000 were produced. The solution was heated to 60°C in order to dissolve all of the polymer and provide a single-phase solution. The polymer solution was fed to the compositional quenching apparatus and heated to a temperature of 290°C just before the flash valve. It was then flashed across a needle valve into a vacuum chamber held at 3.5 Torr. The partially devolatilized product was found to consist of approximately 40% polymer by weight.

The product was then processed to remove the remaining DMF. First, the material was allowed to air-dry at room temperature for 12 h. This was followed by placing the material in a vacuum oven under full vacuum and ramping the temperature from 25 to 180°C over 6 h. The 5% and 10% Viton blends were ground in a mill (Wiley model 3) through a 2 mm sieve to produce a granular material, which was subsequently placed in a vacuum oven for 24 h at 150°C and full vacuum. This material was then passed through a Werner–Pfleiderer (WP) vented, 30 mm, twin-screw extruder to remove the residual solvent. The 15% Viton blend was ground through a 0.5 mm sieve producing a fine powder, which could be dried using the vacuum oven alone. The powder was kept in a vacuum oven at 175°C and full vacuum for 72 h to remove the residual solvent. No differences in particle size or shape were apparent in the compositionally quenched blends despite the different devolatilization techniques.

Blends were also produced by passing well mixed Ultem (90%) and Viton (10%) pellets through a 28 mm WP twin-screw extruder. Compounding was done at screw speeds of 100 and 200 rpm in an effort to produce blends of different rubber particle sizes. In addition, one batch was subjected to two passes through the extruder at 300 rpm (denoted 300(2) rpm).

In addition, a 90/10 Ultem–Viton blend was produced by precipitation of the polymer from solution. A polymer solution similar to the one used as feed for the compositional quenching process was slowly poured into an equal amount of water, an antisolvent, to precipitate the polymer blend from solution. The precipitate was collected by filtration, dried and then processed similarly to the 15% Viton blend produced by compositional quenching.

Before moulding, the compositionally quenched blend and the extruded compounds were dried in an air-circulating oven at 150°C for 5 h. Mini (ASTM type 5) tensile bars and Izod impact test bars were injection-moulded using a 28 ton Engle injection-moulding machine. Moulding was performed using a 325°C nozzle temperature and a heated mould kept at 107°C.

A number of tests were performed on each of the samples in order to characterize their physical properties and assess their relative performance. A TMI Impact Testing Machine model 43-1 was used for the standard Izod impact test. A TMI Monitor/Impact model 43-02 equipped with a controlled-temperature cell was used to measure Izod impact strength over the temperature range of -30 to 175°C. A model TMI-22-05 notching cutter was used to cut notches on all Izod specimens in accordance with ASTM standards. At least five samples were tested in each case with more than 10 samples tested for the mechanically compounded blends. Impact strength values quoted are an average over all tests. Room-temperature tensile tests were done on an Instron Tensile Testing Machine model 1125 equipped with Laboratory Microsystems Inc. 'Mechanical Testing Package 2.1' data analysis software. Yield strength, yield strain, tensile modulus, strength at break and elongation (%) were measured for all samples. At least three tensile tests were performed on each material, with more done if tests provided conflicting results. Tensile tests were done on ASTM type 5 sample bars at a crosshead speed of 0.2 inch min^{-1}. Variable-temperature tensile tests were done on a Instron model 1123 equipped with a model 3111 environmental chamber using a crosshead speed of 0.1 inch min^{-1}. All specimens were allowed to equilibrate at test temperatures for at least 20 min. Extensometers were not employed.

A Perkin–Elmer Thermogravimetric Analyzer (model TGA7) equipped with thermal analysis software (TAS, Version 2.0) was used to assess the thermal stability of the prepared blends as well as the virgin Ultem. Thermogravimetric analysis was performed using a heating rate of 5°C min^{-1}. The weight of the polymer was measured as a function of exposure temperature in these tests. A decrease in weight signifies polymer degradation.

Finally, fracture surfaces and representative cross-sections were analysed by scanning electron microscopy (SEM) using an International Scientific Instruments model IIIA microscope. Fracture surfaces were observed to gain insight into the processes occurring and the differences in fracture between modified and unmodified material. Fracture surfaces analysed by SEM were produced from room-temperature notched Izod tests. Representative cross-sections were also analysed by SEM in order to measure the rubber particle sizes in the prepared blends. Part of an injection-moulded sample was encapsulated in an epoxy bullet. The bullet was then cut using a Sorvall 'Porter–Blum' Ultramicrotome (MT-2) equipped with a freshly cut glass knife. The bullet was then frozen in liquid nitrogen and subsequently polished using the ultramicrotome. It was then soaked in methyl ethyl ketone for 2 h in order to selectively dissolve the Viton A and thus etch the polished surface.

RESULTS AND DISCUSSION

A comparison of the mechanical properties for the experimental materials containing 10% Viton is given in *Table 1*. It is obvious that the addition of 10% Viton A is an effective method to impact-modify Ultem. Virtually a three-fold improvement in Izod impact strength is observed with a 10% addition of Viton A in blends made by both compositional quenching and extrusion (at all screw speeds). This major improvement in impact strength is coupled with a relatively small sacrifice in yield strength and modulus (−16% and −14%, respectively, for the compositionally quenched blend). The precipitated 90/10 blend, meanwhile, did not exhibit any improvement in impact strength over the neat material.

There are significant differences in tensile behaviour between compositionally quenched and extruded blends. Up to the yield point, the blends produced by both methods perform similarly. They have a tensile modulus and yield strength that are virtually the same, and differences are only manifested in post-yield behaviour. The compositionally quenched blend has a much higher strength at break and a larger elongation (%) than any of the extruded blends. There is a clear progression of increasing strength and elongation at break with increasing screw speed in the extrusion blends. This progression is illustrated in *Figure 2*, which shows tensile tests for individual samples of extruded blends of various screw speeds as well as the compositionally quenched (CQ) blend.

The differences in mechanical behaviour of these materials can be linked to their morphological differences. *Figure 3* is a scanning electron micrograph of a polished and etched surface of the compositionally quenched blend. The average rubber particle size in this material is approximately 0.3 μm, with the largest of these particles being 0.5 μm. The particles are generally spherical in shape. On the other hand, all of the extruded materials included particles that were at least twice the size of the largest rubber domains found in the compositionally quenched material. *Figure 4* shows the etched surface of the 200 rpm extruded blend. The rubber domains are substantially larger (≃2.5 μm) than those found in the compositionally quenched blend. In addition, the particles are no longer spherical in shape, but instead highly elliptic. *Figure 5* shows that the rubber particles in the precipitated blend are much larger than in the other materials. The particles are as large as 15 μm

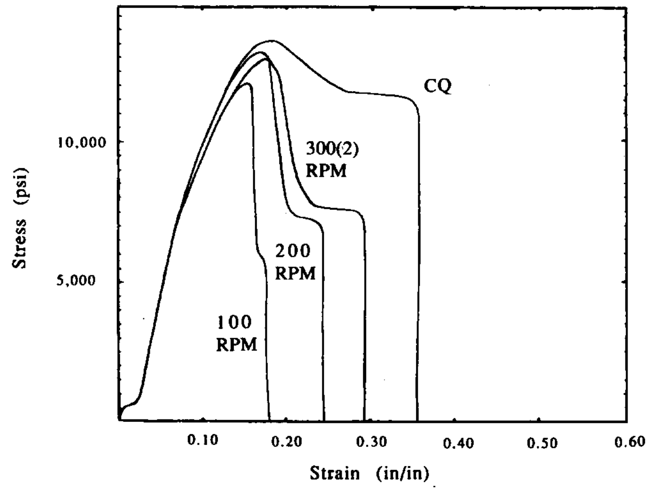

Figure 2 Tensile test stress–strain surves for 90/10 Ultem–Viton blends

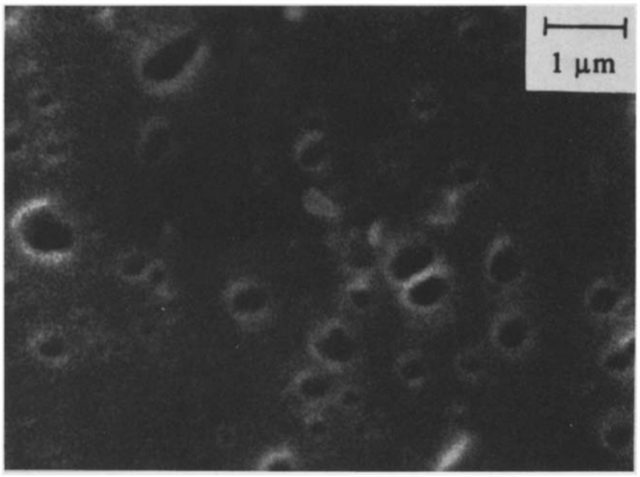

Figure 3 SEM of 90/10 Ultem–Viton blend produced by compositional quenching

Table 1 Mechanical property comparison between Ultem and various 90/10 Ultem–Viton blends

		90/10 Ultem–Viton				
	Ultem 100	Compositional quenching	Extruded, 100 rpm	Extruded, 200 rpm	Extruded, 300(2) rpm	Precipitated
Izod impact strength (ft lb/inch)	0.58	1.51	1.71	1.42	1.46	0.45
Yield strength (psi)	14400	12200	12200	13000	12900	13360
Yield strain (inch/inch)	0.165	0.165	0.155	0.158	0.174	0.184
Tensile modulus (psi)	171500	146700	148200	158100	143100	134200
Strength at break (psi)	15000	10700	6100	7600	7400	11000
Elongation (%)	137	56	20	25	27	34

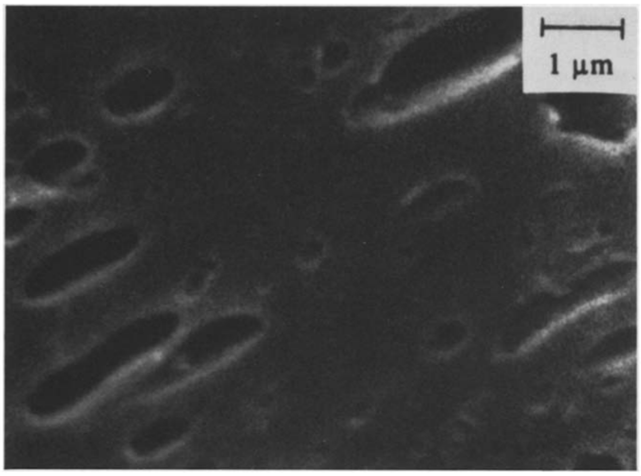

Figure 4 SEM of 90/10 Ultem–Viton blend produced by extrusion (200 rpm)

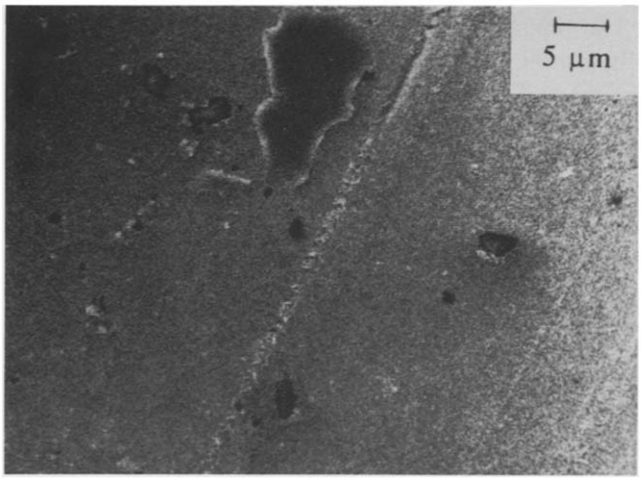

Figure 5 SEM of 90/10 Ultem–Viton blend produced by precipitation

in size. We thus conclude that particles of this size and larger are ineffective as impact modifiers.

Figures 6 and *7* are SEM photographs of fracture surfaces obtained from a room-temperature notched Izod test. *Figure 6* is the fracture surface of neat Ultem, and *Figure 7* shows the fracture surface of the compositionally quenched blend. The extrusion blended materials had fracture surfaces that were quite similar to the one shown in *Figure 6* for the compositionally quenched blend. The fracture surfaces of the blends are quite sinuous and expose a great deal of surface area. In addition, there seems to be shear yielding of the polymer matrix and rubber particle dislocations on these surfaces. In contrast, the neat Ultem fracture surface is quite flat. There is little evidence of shear yielding, and the fracture path seems quite direct. It seems likely that the increased toughness of the blend is due to the tortuous path of the fracture along with the extensive yielding that occurs in the modified material. There is no evidence of crazing, and the rubber particles seem to function as shear yielding initiators[4,5].

These results agree with the findings of Wu[6] for a type II polymer, which has a high crack initiation energy but a low crack propagation energy in impact. Ultem has a high unnotched impact strength, but a low notched impact strength characteristic of a type II polymer. Wu states that these materials are rubber-toughened mainly by increased matrix yielding. Wu proposes, for type II blends, that, when the distance between rubber particles is less than some critical value, the stress fields around the rubber particles interact considerably to enhance matrix yielding and produce tough behaviour. Tough behaviour for 90/10 Ultem–Viton blends corresponds to an impact strength of 1.5 ft lb/inch, approximately three times the impact strength found for brittle fracture. Assuming that the rubber particles are uniformly sized spheres arranged in a cubic lattice, the interparticle spacing T can be calculated from the known particle diameter d and the volume fraction ϕ of the rubber as:

$$T = d[(\pi/6\phi)^{1/3} - 1] \tag{1}$$

Given that the average particle sizes are 0.3, 1.0 and 7.0 μm for the compositionally quenched, extruded and precipitated blends, respectively, we would calculate the interparticle spacings to be 0.22, 0.74 and 5.2 μm, respectively. These values represent gross estimates of the true interparticle spacings since the assumptions behind equation (1) are certainly violated. However, from this we can estimate the critical interparticle distance for Viton-modified Ultem to be of the order of 1 μm in size. The results here also back Wu's contention that strong adhesion between the rubber and matrix phases as provided by chemical bonding is not necessary and that

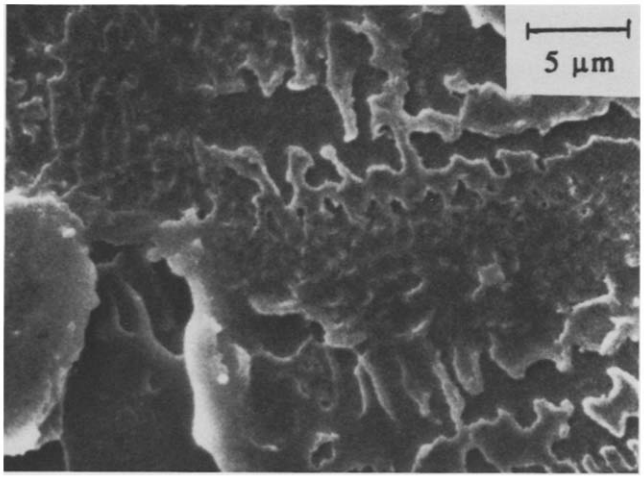

Figure 6 SEM of Ultem fracture surface

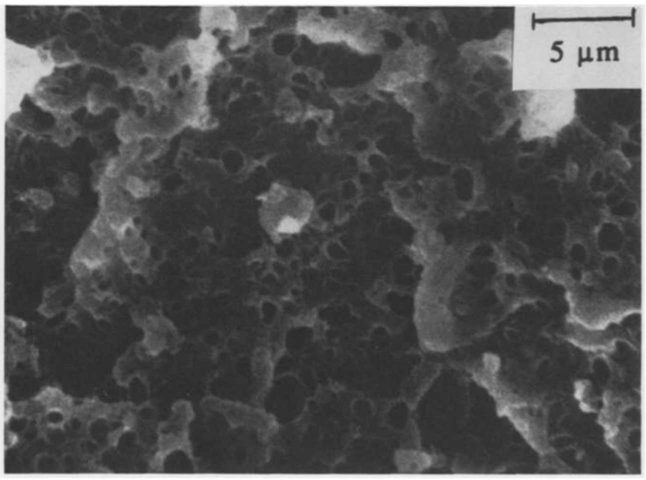

Figure 7 SEM of 90/10 Ultem–Viton blend (CQ) fracture surface

adhesion provided by van der Waals attractions alone is adequate for toughening.

The most important difference observed between the compositionally quenched material and the extrusion blends is that the extruded blends all showed signs of delamination while the compositionally quenched material did not. These delaminations became obvious when the material was twisted. Layer separation and tearing were observed. Delamination in blends is often an indication of incompatibility of the polymers making up the blend. This incompatibility seems to be overcome in the compositionally quenched material, presumably by creating a more intimate mixture of the two polymers. Using low-magnification SEM, *Figure 8* shows the skin of oriented polymer present on the surface of a test bar made from a blend produced by compounding. This type of skin is characteristic of a delaminating material. The blends produced through the process of compositional quenching did not contain such a skin.

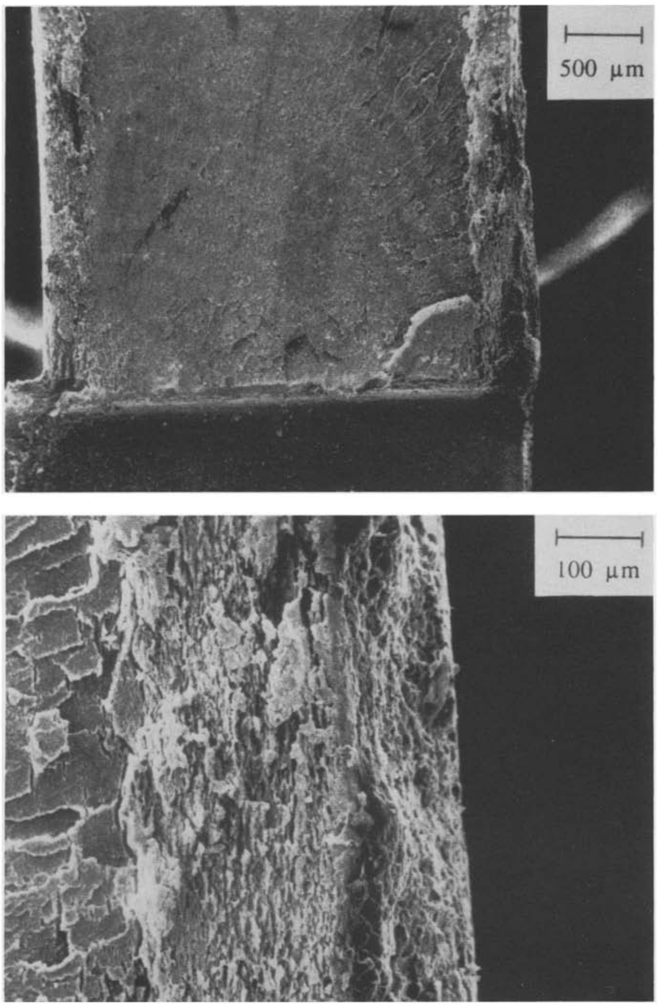

Figure 8 Low-magnification SEM of 90/10 Ultem–Viton blend produced by extrusion

Table 2 shows the measured mechanical properties of neat Ultem along with Ultem–Viton blends containing 5, 10 and 15% Viton. The blends were produced via compositional quenching. The average rubber particle size in all of these blends was slightly less than a half of a micrometre, approximately 0.3 μm in diameter. The impact strength of the blends increases with rubber content. These impact strengths all seemingly correspond to 'tough' behaviour, under Wu's tough–brittle transition framework[6], even the blend containing 5% Viton, which shows only a modest improvement in impact strength. The interparticle distance in the 5% Viton blend is approximately 0.4 μm, which is less than the apparent interparticle distance in the extrusion compounded 10% Viton blend, which exhibits tough behaviour.

The increase in impact strength with increasing amounts of added rubber is believed to be due to the activation of shear yielding deformation in a larger volume of the matrix material surrounding the crack tip. Rubber inclusions are well known to act as stress concentrators in the matrix material immediately surrounding the particle[7,8]. An intense concentration of stress exists in the region about the tip of a propagating crack[9]. The rubber particles in the vicinity of the crack tip act as a larger number of nucleation sites for expanding stress concentration regions. These induced stress fields extending from the surface of the rubber particles interact appreciably when the particles are close enough together so as to create a relatively large region of high stress. The rubber particles thus act as stress relaxation agents, which transforms a small area of intense stress at the tip of a propagating crack in an unmodified material to a much larger region of comparably lower stress that is able to initiate and sustain energy-absorbing deformation processes in a modified material. The occurrence of deformation processes such as shear yielding and crazing results in a higher measured impact strength.

The results of tensile tests given in *Table 2* show that sacrifices in modulus and yield strength must be accepted as a tradeoff for improved impact strength in blends having a higher rubber content. A decrease in modulus and yield strength of approximately 7% was found for each 5% increase in rubber content. These decreases, however, are modest in comparison to the dramatic increases observed in impact strength.

The improvement in impact strength of the rubber-

Table 2 Mechanical properties of Ultem–Viton blends of various rubber contents

	Ultem 1000	95/5 Ultem–Viton: compositional quenching	90/10 Ultem–Viton: compositional quenching	85/15 Ultem–Viton: compositional quenching
Izod impact strength (ft lb/inch)	0.58	0.70	1.42	1.96
Yield strength (psi)	14400	13800	12200	11700
Yield strain (inch/inch)	0.165	0.166	0.165	0.171
Tensile modulus (psi)	171500	162800	146700	136500
Strength at break (psi)	15000	10200	10700	10000
Elongation (%)	137	26	56	41

Table 3 Mechanical properties of Ultem and 85/15 Ultem–Viton at various temperatures

	Ultem				85/15 Ultem–Viton			
Temperature (°C)	−30	20	100	175	−30	20	100	175
Izod impact strength (ft lb/inch)	0.50	0.49	0.42	0.39	0.64	1.96	2.93	13.85
Yield strength (psi)	19 000	14 800	9 000	4 200	17 000	12 900	7 400	3 100
Yield strain (inch/inch)	0.180	0.159	0.130	0.080	0.180	0.162	0.135	0.075
Tensile modulus (psi)	196 000	178 000	138 000	104 000	198 000	144 500	110 000	77 000
Strength at break (psi)	16 300	13 700	8 100	3 700	14 600	10 800	7 700	3 700
Elongation (%)	78	96	106	113	19	33	88	137

modified materials in comparison to the neat matrix material is even more dramatic at elevated temperatures. *Table 3* compares the Izod impact strength of neat Ultem with that of the 85/15 Ultem–Viton blend over the temperature range of −30 to 175°C. The impact strength of the neat resin is essentially temperature-insensitive over this range. The impact strength of the blend approaches that of the neat material for low temperatures. This result is expected since the rubber will essentially act as a glass at these temperatures and the fracture will proceed directly through the glassy particles. The glass transition temperature of Viton A was found to be −19°C using differential scanning calorimetry. At elevated temperatures, the situation is quite different. The rubber-modified material exhibits a dramatic increase in impact strength above 100°C. In fact, the impact strength of the blend is approximately 30 times greater than that of the neat resin at 175°C. Interestingly enough, the impact strength of the blend at these elevated temperatures approaches the unnotched Izod impact strength of the neat resin. The combination of elevated temperature and added rubber particles act together essentially to blunt the crack tip.

Figure 9 shows the fracture surface created from an Izod impact test at the 85/15 Ultem–Viton blend performed at 175°C. The increase in temperature causes an even larger volume of the matrix material to be involved in the shear yielding deformation about the crack. This should be expected since the yield strength of the matrix material drops significantly with increasing temperature. This allows stresses further from the crack tip to cause matrix yielding.

Bucknall and Street[10] have previously observed this type of increase in impact strength with increasing temperature for HIPS, modified PMMA and modified PVC. They concluded that this behaviour was due to the activated initiation of crazes in the matrix phase, which effectively relaxes the stress field about the tip of an advancing crack. In Ultem–Viton blends, there is no evidence of crazing, and shear yielding is believed to be the major deformation process occurring in the type II[6] matrix material. Higher temperatures allow shear yielding to occur in regions further from the crack tip, which are at lower stress levels since the yield strength of the matrix has been lowered. The same stress field relaxation arguments used by Bucknall and Street apply to this shear yielding polymer situation. Additional energy is absorbed by the yielding matrix material during the fracture of the blend. This results in a higher measured impact strength.

Table 3 also shows the tensile properties of neat Ultem and the 85/15 Ultem–Viton blend at a series of temperatures between −30 and 175°C. Several interesting aspects of this comparison are evident. The moduli of both the blend and the neat resin are essentially the same at −30°C while at the higher temperatures the blend has a modulus that is approximately 20% lower than that of the unmodified polymer. Again the explanation for this phenomenon is that the rubber is essentially a glass with a modulus similar to the matrix material at the low temperature while at the higher temperatures the modulus differences between the two phases becomes significant.

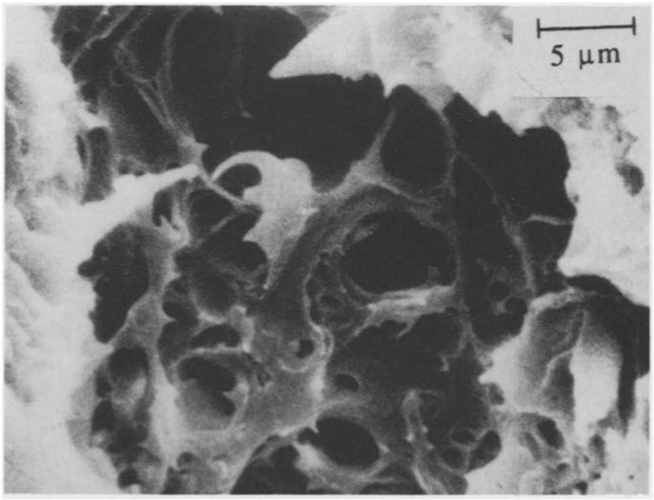

Figure 9 SEM of 85/15 Ultem–Viton blend fracture surface created at 175°C

In addition, the ultimate elongation of these materials shows an interesting dependence on temperature. The neat resin has a relatively high elongation even at low temperatures. The blend, meanwhile, elongates significantly less at temperatures at or below ambient. At higher temperatures, however, the elongation drastically increases and even surpasses that of the neat polymer. The increased ability of the matrix to cold flow and yield at high temperatures so as to heal the molecular separations that are created in tension allows the material to elongate to a higher degree. In essence, the flaw sensitivity of the matrix is drastically reduced at elevated temperatures. The flaws inherent at the particle–matrix interface in the rubber-modified materials thus become less destructive at these elevated temperatures.

Figure 10 shows the results of the thermogravimetric analyses. There were no observable differences in thermal stability between the compositionally quenched and extruded blends. There is some loss of thermal stability in these rubber-modified materials as seen from the earlier weight loss in comparison to the neat Ultem. However,

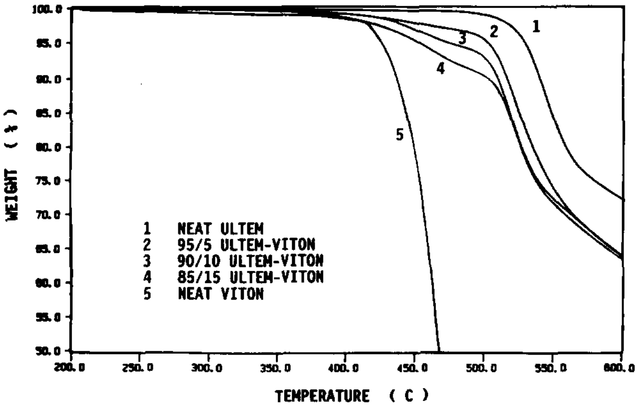

Figure 10 Thermogravimetric analysis of Ultem, Viton and Ultem–Viton blends produced by compositional quenching

this loss of weight in the blend does not occur until about 425°C.

CONCLUSIONS

A new impact-modified high-temperature blend has been produced. The addition of 10% Viton A to an Ultem poly(ether imide) matrix by the process of compositional quenching increases the impact strength by nearly a factor of 3 with little sacrifice in modulus, strength and thermal stability in comparison to the neat Ultem. The addition of 15% Viton results in approximately a four-fold improvement in impact strength. Rubber particles formed in this process are spherical in shape with a diameter of approximately 0.3 μm. The particles are not chemically bonded to the matrix. Adhesion due to van der Waals forces is sufficient for toughening in this system. The rubber particles seem to act as shear yielding initiators since extensive yielding is apparent on the fracture surfaces of the blends and not on the pure material. These findings agree with the work of Wu for a type II matrix and suggest that the critical interparticle distance for the toughening of Ultem is of the order of 1 μm in size. The compositionally quenched material outperforms conventionally blended materials, which were found to have inferior post-yield tensile behaviour and suffer from delamination.

A 10% Viton blend formed by precipitation did not exhibit any improvement in impact strength. The particles in the precipitated blend were substantially larger than in the other blends, approximately 10 μm in diameter. For a given rubber content, particle size does not seem to affect the impact strength of the blend until the particles become so large that they are completely ineffective at toughening the material. This supports the work of Wu, which identified a similar tough–brittle transition for modified nylon.

All of the compositionally quenched Ultem–Viton blends exhibited what is believed to be tough impact failure. The impact strength of these blends increased with rubber content. The increased amount of rubber seems to cause greater amounts of the matrix material to experience energy-absorbing deformation.

The improvement in impact strength of these materials becomes more evident at elevated temperatures. Whereas the neat polyimide has a relatively constant impact strength with respect to temperature, the rubber-modified blend shows dramatic improvement in impact strength with increasing temperature. Observation of the fracture surface produced at these elevated temperatures provides evidence that yielding is much more extensive than at ambient conditions. At high temperatures, the impact strength of the 85/15 blend approaches the unnotched impact strength of the neat resin. The rubber particles function as shear yielding initiators while the increased temperature lowers the yield strength of the matrix material. The combination of these two phenomena causes yielding to occur in a relatively large volume surrounding the tip of a propagating crack and effectively relaxes the stress concentration at the crack tip. This action essentially blunts the crack tip.

ACKNOWLEDGEMENTS

This work was funded by contracts from the Army Research Office and the New York State Science and Technology Foundation. The support from General Electric through gifts and use of their facilities was instrumental in this study.

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