Toughening of Epoxy Resins Modified with Polyetherester Block Copolymers: The Influence of Modifier Molecular Architecture on Mechanical Properties

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ABSTRACT: Thermoplastic elastomers based on polyetheresters with polyoxytetramethylene soft segments and poly(hexamethyleneterephthalate) hard segments were used to toughen anhydride-cured epoxy resins. The ratio between hard and soft segments and the crystallinity of the hard segments prepared by incorporating poly(hexamethyleneisophthalate) in the block copolymer were varied in order to examine the effect of the modifier's molecular architecture on morphology and mechanical properties of the resin, such as toughness, strength, and stiffness. The experimental data show that segmented polyetheresters are suitable toughening agents for epoxies. The compatibility between resin and toughener and also the mechanical properties of the modified resin depend on the ratio between the hard and soft segments. Epoxy resins blended with 10 wt % of the polyetherester exhibit an increase in toughness by 50–150%, while strength and modulus decrease by 20% or less. An optimal phase adhesion at levels between 70 and 85 wt % of soft segments in the modifier results in a maximum of toughness enhancement (by about 150%) of the resin accompanied with only a slight drop in strength and stiffness (by about 15%). The glass transition temperature is only slightly affected. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 623–634, 2000

Key words: epoxy resin; mechanical properties; morphology; polyetherester; segmented block copolymers; thermoplastic elastomer; toughening

INTRODUCTION

Highly crosslinked thermosets are well known to exhibit structural stiffness and dimensional stability. Among thermosets, epoxy resins combine good processability with excellent cost performance. On the other hand, epoxy resins, like most other thermosets, are highly brittle and notch sensitive. This deficiency, mainly caused by high network density, is crucial especially in the case of safety-oriented applications such as structural automotive parts or modern laminated construction systems. To improve competitiveness with respect to other engineering materials, it is important to enhance toughness of epoxy-based materials.

Toughness is directly related to the energy necessary to initiate and propagate a crack. To increase the toughness of a given polymeric system, it is necessary to enhance the ability of this system to consume the energy responsible for crack

initiation or propagation. This energy usually originates from external forces during impact or stress sensations, but it can also originate from an internal stress buildup due to temperature changes, solvent contacts, or degradation processes within the polymer. The main strategy of toughness enhancement is based on the dispersion of one or more impact modifiers in the epoxy matrix. These impact modifiers can be oligomers, polymers, inorganic fillers, or combinations thereof.[1] Processes must be initiated by these modifiers to consume energy beyond the energy consumption of the unmodified polymer. These processes can take place within the impact modifier particles and the small interfacial area between impact modifier and matrix or within the matrix resin. Typical deformation processes within the particulate modifiers in epoxy resins are cavitation and tear, but many others are possible, and have been proposed.[2] On the other hand, only two matrix deformation processes have been proposed over the years: microfibrilation—also called crazing—and shear yielding. Although crazing is believed to be impossible in epoxy systems, several authors have suggested a similar process referred to as "pseudocrazing," which has been the focus of some controversy. Nonetheless, matrix deformation processes seem to rely heavily on the stress conditions within the matrix.

Stress concentrations at the particle–matrix interface play a key role in the initiation of global deformation processes. The higher the stress concentration at the interface, the more likely the yield stress maximum of the matrix will be exceeded, resulting in a matrix deformation process and a higher toughness. If the particle-to-matrix adhesion is not suitable enough, a delamination of the particle from the matrix will occur before the yield stress level for the matrix polymer can be achieved.

Many different classes of impact modifiers, such as inorganic fillers, thermoplastics, core-shell particles, or reactive liquid rubbers, have been successfully applied to brittle epoxy systems. Carboxyl-terminated butadiene/acrylonitrile copolymers (CTBN), for example, are very successful impact modifiers because their solubility in various polymers can be controlled by varying the butadiene and acrylonitrile ratio.[3] Other similar impact modifiers have also been synthesized and used in epoxy resins.

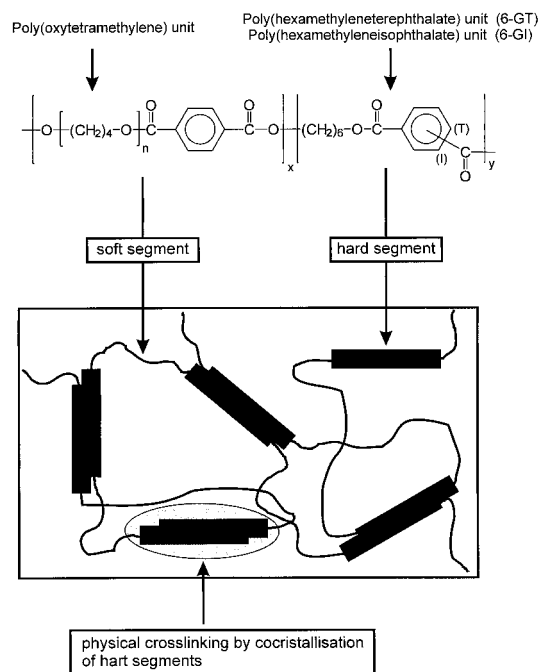Among oligomeric elastomers, block copolymers are of particular interest. As a function of block copolymer molecular architectures, especially the content of soft and hard segments, it is possible to control morphology development during cure. Block copolymers containing flexible segments represent thermoplastic elastomers where hard segments form thermally reversible crosslinks via intermolecular interactions of the hard segments. This network formation is shown in Figure 1 for crystalline hard segments. The first reports of blending epoxy resins with polyetherester thermoplastic elastomer impact modifiers date back to 1973 by Hoeschel.[4] His high molecular weight polyetheresters contained poly(tetramethylen oxide) soft segments and poly(butylene terephthalate) hard segments. Styrene–Butadiene–Styrene thermoplastic elastomers (Kraton®) have also been reported to be good impact modifiers for epoxy resins.[5]

The purpose of this work is to examine low and high molecular weight polyetherester block copolymers as impact modifiers for epoxy resins based on Bisphenol A–diglycidylether and hexahydrophthalic anhydride. Although many commercial block copolymers[6] of this type are available, it was decided that all polyetherester block copolymers should be synthesized for good reproducibility and to establish structure/property correlations via systematic variation. Moreover, all sam-

Figure 1 Concept of thermoplastic elastomers composed of a segmented polyetherester block copolymer (schematic).

ples were purified to exclude effects of additives and polycondensation catalysts, which are likely to be present in commercial polyetheresters such as HYTREL®.

Most commercial polyetheresters contain poly(tetramethylene terephthalate) (4-GT) as hard segments. Because preliminary experiments indicated better compatibility of the poly(hexamethylene terephthalate) (6-GT) with the epoxy system, it was decided to prepare polyetheresters with 6-GT hard segments. According to Peters and coauthors[7] crystallinity of 6-GT–based is very similar to those of 4-GT–based polyetherester. To study the influence of the hard segment crystallinity copolyester hard segments containing 1 mol/1 mol mixture of isophthalic and terephthalic acid (6-GI/T) were used in addition to 6-GT.

MATERIALS

Polyetheresters

All polyetherester syntheses followed a standard procedure based on low temperature polycondensation ($-10°$C) of terephthaloyldichloride or a 1 : 1 ratio of terephthaloyldichloride and isophthaloyldichloride and a mixture of hexanediol and dihydroxy-terminated poly(oxytetramethylene). The poly(oxytetramethylene)[8] used has a molecular weight of 2000 g/mol (POTM 2000). Chloroform was used as solvent. Pyridine was used as scavenger for the hydrochloric acid that was formed during the polycondensation reaction. All polyetheresters synthesized were carefully purified to remove excess pyridine and pyridinium hydrochloride, which act as catalysts for the epoxy resin. Thus, the reaction solution was poured in a 3 : 1 ratio mixture of methanol and water with 5% acetic acid. To ensure an appropriate emulsification, a lab dissolver (Ultraturrax form Ika) was used. The polymer was filtered and the process was repeated two more times. After drying the polyetherester over magnesium sulfate, it was dissolved again in chloroform. This solution was treated with an acidic ion exchanger (Amberlyst 15 from FLUKA), and then filtered and dried.

The number-average molecular weight M_n was determined by means of vapor pressure osmosis.

Hard-to-Soft Segment Ratios

The hard-to-soft segment ratio of polyetheresters was determined with ^{1}H-NMR analysis in a Spektranet-Bruker ARX 300 system: the signal intensities of methylene protons next to an ester oxygen at $\delta = 4.3$ ppm have to be compared with the signals of methylene protons next to a ether oxygen at $\delta = 3.4$ ppm. Because the molecular weight of the poly(oxytetramethylene) that was used to build the soft segment is known, the ratio between soft and hard segments can be calculated from these signals. In Table I, soft-to-hard segment ratios of the synthesized polyetheresters are displayed.

Thermal Behavior

The thermal behavior of the polyetheresters was determined using a Perkin-Elmer DSC-7. To ensure the reproducibility of the data, all samples were annealed at 140°C for 20 min, followed by defined cooling at a rate of 10 K/min. The data were taken at the following heating run at 20 K/min and were used for data acquisition. As can be seen from Table I as well as from Figures 2 and 3, the different hard-to-soft segment ratios in the polyetheresters strongly control the thermal behavior. In contrast to the soft segment melting temperatures, which are hardly influenced by the hard-to-soft segment ratio, the hard segment melting temperatures increase proportionally with the hard segment content.

The difference between the hard segment crystallinities for both the 6-GT and the 6-GI/T series can clearly be resolved: the hard segment melting temperatures for the higher crystalline 6-GT series polyetheresters exceeds the equivalent melting temperatures of the 6-GI/T series by 40°C or more (Table I). It can also be seen that polyetheresters with more than 70% hard segment content are capable of forming thermoplastic elastomers because there is no soft-segment melting point for these polyetheresters observable.[9]

Epoxy Resins and Blends thereof with Polyetherester Copolymers

For this investigation a commercial epoxy resin based on Bisphenol A–diglycidylether was used. The epoxy resin (GY 250, Ciba-Geigy) was mixed with hexahydrophthalic anhydride (HT 907, Ciba-Geigy). The ratio of GY 250 and HT 907 was 4 : 3. The epoxy resins were modified with 10 wt % of the polyetherester block copolymers that was previously synthesized. 1 wt % of the resin/hardener system was calculated to determine the amount of N,N-dimethylbenzylamine (DY 062,

Table I Characterization Data of the Polyetheresters Synthesized

T/I[a] (% : %)	Soft Segment[b] (wt %)	Hard Segment[b] (wt %)	M_n[c] (g/mol)	M_w/M_n[d]	T_g Soft[e] (°C)	T_m Soft[f] (°C)	T_m Hard[g] (°C)
50 : 50	0	100	6180	2.6	12	—	94
50 : 50	22	78	5150	2.4	−15	—	70
50 : 50	38.5	61.5	5500	2.0	−31.3	—	76
50 : 50	60	40	4520	2.1	−37	—	74
50 : 50	69	31	4850	2.1	−61.5	18.3	44
50 : 50	82	18	5340	2.0	−64	14	55
50 : 50	86	14	5120	2.1	−69	23	—
50 : 50	94	6	4680	1.9	—	22	—
50 : 50	97	3	5890	2.2	—	—	—
50 : 50	100	0	4750	2.2	−61	28	—
100 : 0	0	100	4300	1.8	—	—	157
100 : 0	15	85	3700	1.9	—	25	142
100 : 0	28	72	4200	2.2	−20	17	142
100 : 0	41.5	58.5	6030	2.3	−50	40	140
100 : 0	50.5	49.5	6010	2.2	−69	16.5	136.6
100 : 0	76	24	5060	2.7	−66	15.5	124
100 : 0	86	14	5280	2.5	−63	26.5	101.8
100 : 0	89	11	4980	2.4	69	17	100
100 : 0	90	10	5300	2.7	−62	18.5	93
100 : 0	93	7	4850	2.6	−67	23.6	—
100 : 0	100	0	5670	2.5	−65	46	—

[a] Terephthalate-to-Isophthalate ratio of the polyetherester.
[b] Hard/soft-segment contents taken from ^{1}H-NMR measurements.
[c] Number-average molecular weight determined by osmometric investigations with CHCl$_3$ as solvent (VPO).
[d] Polydispersity determined from GPC measurements using CHCl$_3$ as solvent.
[e] Glass transition temperature (T_g) of the soft segment as measured by DSC.
[f] Melting temperature of the soft segment as measured by DSC.
[g] Melting temperature of the hard segment as measured by DSC.
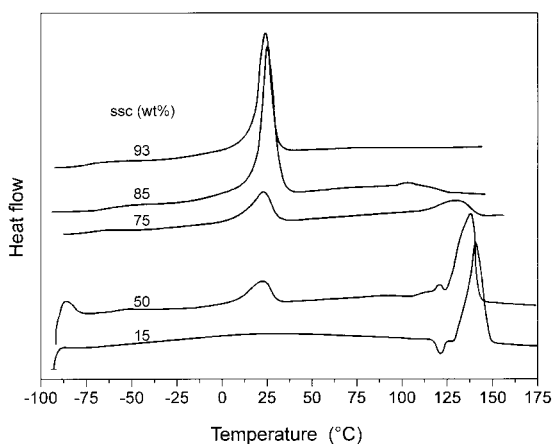
Figure 2 Thermal transitions (DSC) of some polyetheresters based on terephthalic units (6-GT series). PEE10: 93 wt % ssc; PEE7: 85 wt % ssc; PEE6: 75 wt % ssc; PEE5: 50 wt % ssc; PEE2: 15 wt % ssc; and ssc = soft-segment content.
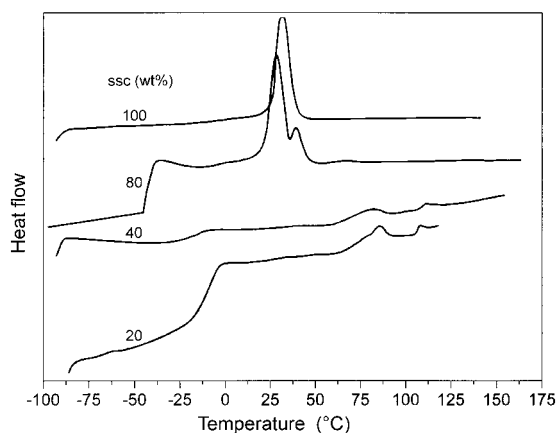
Figure 3 Thermal transitions (DSC) of some polyetheresters based on a 1 : 1 mixture of terephthalic and isophthalic units (6-GI/T series). PEE20: 100 wt % ssc; PEE17: 80 wt % ssc; PEE14: 40 wt % ssc; PEE13: 20 wt % ssc; and ssc = soft-segment content.

Ciba-Geigy) accelerator to be used. GY250, HT 907, and the polyetherester modifier were blended for 45 min at 80°C. To minimize the gas loading the blend was homogenized by mixing in vacuum at 20 mbar. After addition of DY 062, the blend was homogenized again for 3 min and transferred into a release-agent–treated mold preheated to 90°C. The crosslinking reaction occurred in an air-circulated oven during a heating cycle of 3 h at 150°C and 1 h at 180°C. To minimize internal stresses within the resin, the process oven was allowed to cool down to room temperature overnight before removing the blends from the oven.

TESTING

Tensile Modulus and Tensile Strength

Tensile tests were performed at a temperature of 23°C and 40% relative humidity in a standard tensile testing machine from Zwick. The test protocol as well as the test specimens were based on DIN 53455.

Fracture Toughness K_{Ic}

To determine the fracture toughness K_{Ic}, pre-cracked compact tension specimens (CT) were used. The strain rate was 5 mm/min. The maximum load P at the breaking point was used to evaluate K_{Ic} using eq. (1).

$$K_{Ic} = \frac{P \cdot (2W + a) \cdot Y}{B \cdot (W - a)^{3/2}} \qquad (1)$$

where W is the specimen width; B is the specimen thickness; a is the initial crack length; and Y is the geometry correction factor.

Dynamic Mechanical Analysis (DMA)

DMA was performed using a Rheometrics Solids Analyser RSA II equipped with a dual cantilever specimen mounting tool. Storage modulus E', loss modulus E'' and loss tangent tan δ were recorded applying a frequency of 1 Hz at a strain level of 0.1% and scanning a temperature range from −100 to +150°C at a heating rate of 5 K/min. The α-maximum of the E'' curve was taken to estimate the glass transition temperature, T_g.

Morphological Evaluation

Scanning Electron Microscopy (SEM)

All SEM investigations were performed using a CamScan SC 24 instrument scanning the fracture surfaces of tensile test bars broken during tests at room temperature. To prevent electrostatic charge of the specimens and to stabilize the morphological features on the fracture surfaces, all specimens were coated with a copper layer by low-energy sputtering[10] at a vacuum of 3×10^{-4} bar. The SEM images were taken in vacuum at 2×10^{-4} bar and at an accelerating voltage of 25 kV.

Transmission Electron Microscopy (TEM)

Thin films were prepared at room temperature with a Reichert-Jung Ultracut E. The cutting speeds were 0.3 to 0.5 mm/s, the cutting angle was 6°. The resulting thin films had a median thickness of 40 to 60 nm (color gray to silver), and were prepared on micronets (Science Services G600HH). Additionally RuO_4 was used to enhance the contrast of the specimens. The microscope used was a Zeiss CEM 902. The acceleration voltage during the tests was 80 kV.

RESULTS AND DISCUSSION

The phase behavior of the polyetherester/epoxy blends was determined by dynamic-mechanical analysis (DMA). Two major transitions can be observed in polyetherester/epoxy blends: the glass transition temperature (T_g) of the epoxy resin and a broad shoulder at −60°C, which is related to ring movements within the Bisphenol A structure. The T_g of the polyetherester's soft segment units, which are supposed to appear between −60 to −70°C, cannot be detected, most likely due to the dominant Bisphenol A shoulder. Additionally, the network density can be estimated as the mean molecular weight M_c between two entanglement points using data taken from DMA spectra approximately 40 K above T_g applying the following formula:

$$M_c = \frac{\Phi \cdot \rho \cdot R \cdot T}{G_e} \qquad (2)$$

or

Table II   Dynamic-Mechanical Characterization of Epoxy Resins, Modified with 10 wt % of Polyetherester Modifiers

Soft Segment[a] (wt %)	T_g[b] (DMA) (°C)	E'[c] $\times 10^7$ (Pa)	M_c[d] (g/mol)
Unmodified epoxy resin			
	120	1.6	810
Epoxy resins, modified with polyetherester modifiers with terephthalate-to-isophthalate ratio 100 : 0			
30	114	1	1278
40	111	1.2	1058
50	115	1	1281
75	120	1	1296
85	118	1	1290
90	114	1.1	1162
90	114	1	1278
93	118	1	1290
Epoxy resins, modified with polyetherester modifiers with terephthalate-to-isophthalate ratio 50 : 50			
20	113	1.2	1063
40	103	1.5	830
60	119	1.2	1077
70	118	1	1290
80	116	1	1284

[a] Soft-segment content of the polyetherester modifier.
[b] Glass transition temperature of the epoxy matrix.
[c] Storage modulus.
[d] Molecular weight M_c between two entanglement points of the network.

$$M_c = \frac{3\Phi \cdot \rho \cdot R \cdot T}{E'} \quad (3)$$

where Φ is the front factor, T is the temperature (K), G_c is the shear modulus, ρ is the density, R is the gas constant, and E' = storage modulus.

As can be seen in Table II, the addition of 10 wt % polyetherester block copolymer modifier does not result in a significant decrease of the glass transition temperature of the resulting epoxy blends. T_g has dropped by 1 to 7 K only compared to T_g of the unmodified resin at 120°C. On the other hand, the modification resulted in an increase of 20 to 40% of the molecular weight between two entanglement points in the network. Neither the T_g nor the molecular weight between two entanglement points can be used to resolve the differences in the hard-to-soft segment ratio or the hard-segment crystallinity of the polyetheresters.
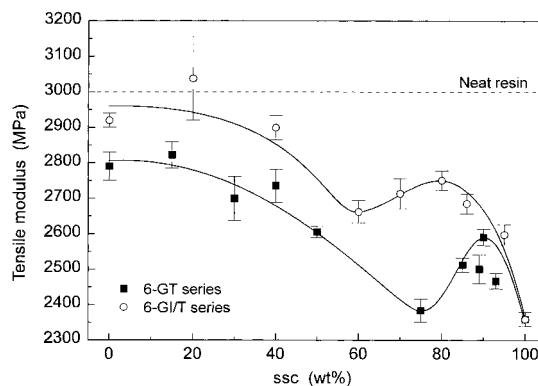
Figure 4   Tensile modulus of epoxy resins, modified with 10 wt % polyetherester blockcopolymers.

In addition to the dynamic-mechanical tests, uniaxial tensile tests were used to reveal differences between the hard-segment crystallinity and the hard-to-soft segment ratio of the polyetheresters based on the stiffness and tensile strength of epoxy resins at a constant modifier content of 10 wt %. As can be seen from Figures 4 and 5, tensile modulus and tensile strength decrease with increasing soft-segment content in the polyetheresters. This general trend can be observed for both the terephthalate-based polyetheresters (6-GT series) and the terephthalate/isophthalate-based polyetheresters (6-GI/T series). However, both series show a peak in the range of 60 to 95% soft-segment content.

To characterize the toughness of the resins, low-speed (static) fracture toughness tests (K_{Ic}) were performed. The curves in Figure 6 exhibit a similar relationship between the soft-segment content in the modifier and the fracture toughness for both series of oligomeric polyetherester
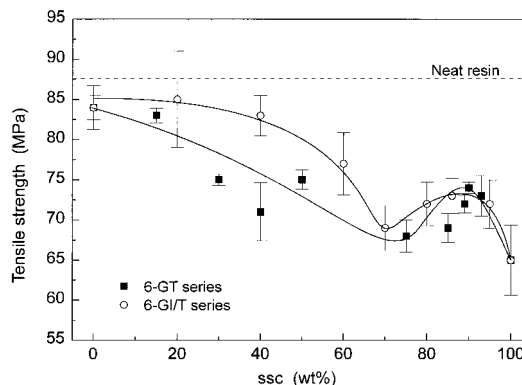
Figure 5   Tensile strength of epoxy resins, modified with 10 wt % polyetherester blockcopolymers.
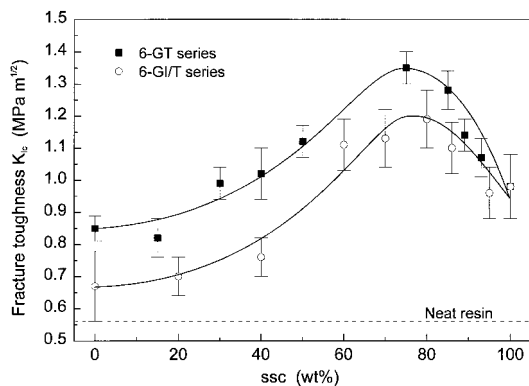
Figure 6 Fracture toughness (K_{Ic}) of epoxy resins, modified with polyetherester block copolymers.

modifiers (6-GT and 6-GI/T). A distinct improvement in toughness can be seen at a loading level of 10 wt % modifier in the epoxy resin using polyetherester modifiers with soft-segment content (ssc) between 40 and 100% having a maximum at about 80%. This dependence of static fracture toughness K_{Ic} on modifier composition is well in agreement with that of dynamic fracture toughness K_{Id}, as published recently.[11]

It is also possible to differentiate the hard-segment crystallinities of the 6-GT and the 6-GI/T modifier series clearly. When averaged statistically, the 6-GI/T-modified epoxy resins demonstrate K_{Ic} values that are roughly 15–20% lower than the corresponding K_{Ic} values for the 6-GT modified epoxy resins.

To determine whether this peak area is due to either the block structure of the polyetheresters causing partial physical network formation or to a solubility effect caused by different solubilities of polyether and polyester blocks in the epoxy resin, an additional test was performed. Mixtures of poly(hexamethylene terephthalate), with an average molecular weight of 1000 g/mol (PHT 1000), and poly(oxytetramethylene), with an average molecular weight of 2000 g/mol (POTM 2000) without covalent chemical connection between the "blocks," were blended into epoxy resin. The ratios of these oligomers were adapted to match the hard-to-soft segment ratios in the polyetheresters. There are linear relations between both tensile strength and fracture toughness of the resin, and poly(oxytetramethylene) content of the modifying mixture. In Figure 7 the results of the K_{Ic} measurements of the mixture-modified resins are exhibited together with the corresponding results of the polyetherester-modified resins (6-GT

series). This shows that the peak area relates to a block copolymer-specific interaction with the epoxy matrix.

Morphology Investigations

Both the transmission electron microscope (TEM) and the scanning electron microscope (SEM) were used to examine the morphological characteristics of the blends. Both confirmed the visual impression that the polyetherester modifier becomes less soluble in the epoxy resin matrix as the percentage of soft segment in the modifier increases.

The TEM images of 6-GI/T-modified epoxy resins are shown in Figures 8(a)–(d). The polyetherester modifiers of the thin films depicted have soft segment contents (ssc) of 20 wt % [Fig. 10(a)], 60 wt % [Fig. 8(b)], 80 wt % [Fig. 8(c)], and 100 wt % [Fig. 8(d)], respectively. With the exception of the sample with 20 wt % ssc, all other thin films reveal holes, caused by tearing out particles during the cutting process. As ssc increases, the particle or hole diameter increases correspondingly. This was confirmed by the statistical analysis of the micrographs (see Table III): the average particle diameter increases from 0.27 μm at a ssc of 60 wt % to values of approximately 0.6 μm in the samples with higher ssc. Apparently, the median particle diameter of the resin with 80 wt % ssc is larger than the particle diameter of the resin with 95 wt % soft segment in the modifier. In addition, the particle surface area of the 80% ssc resin a relatively higher contribution to the total surface area of the sample. The contribution of the parti-
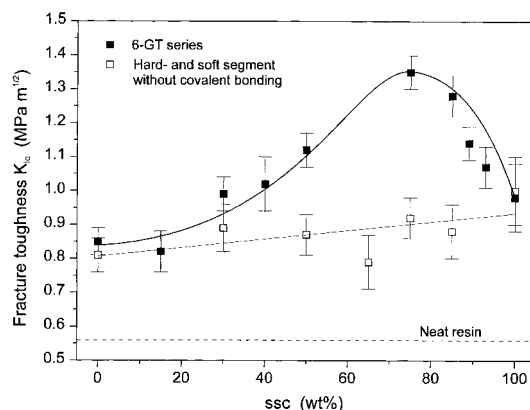

Figure 7 Fracture toughness (K_{Ic}) of the epoxy resin modified with a mixture of hard (PHT 1000) and soft segments (POTM 2000) without covalent chemical bonding compared to the corresponding results of the polyetherester modified resin.
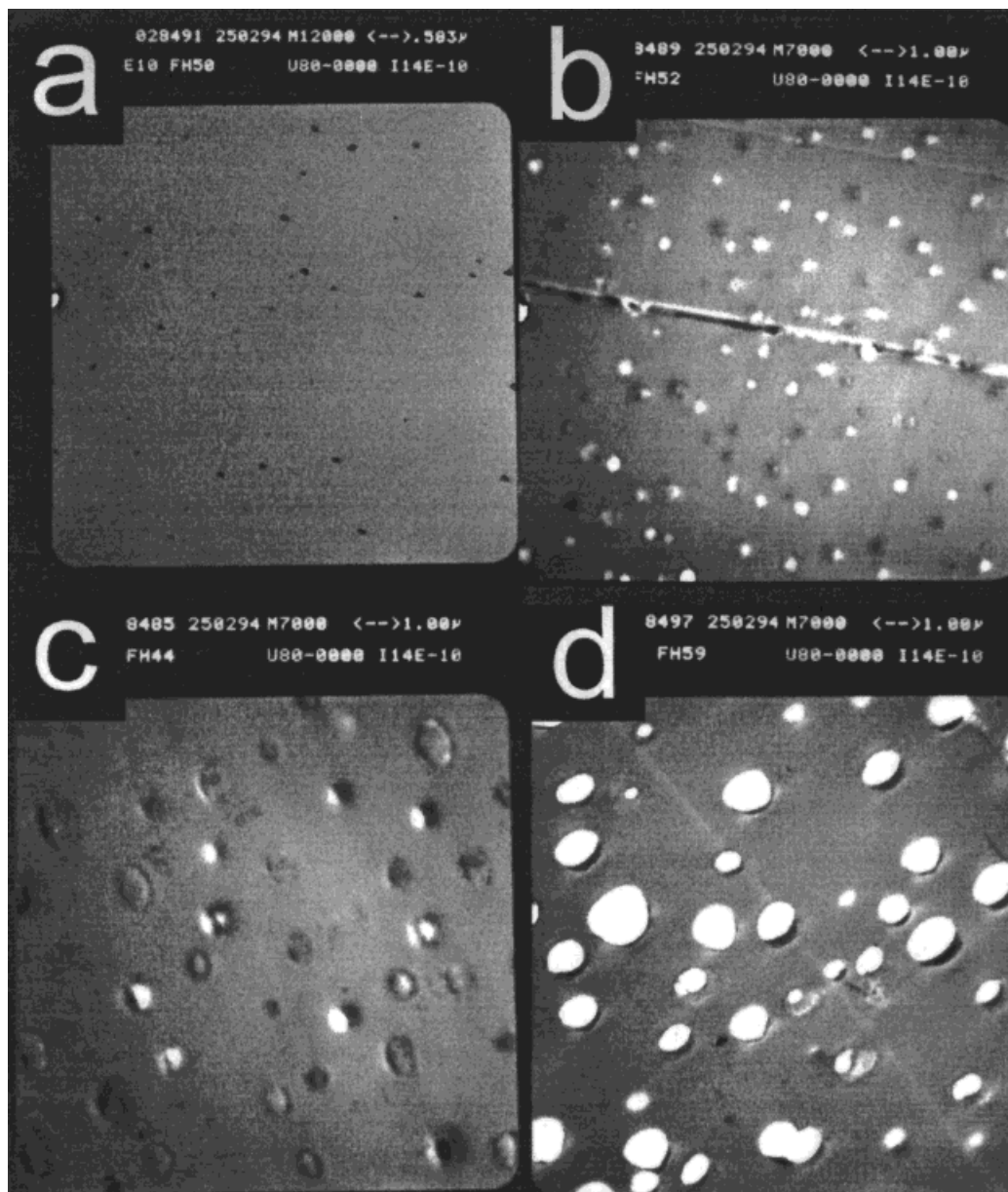
Figure 8   Elastic bright-field micrographs (TEM) of epoxy/polyetherester (6-GI/T serie) blends. (a) 20 wt % soft-segment content (PEE13); (b) 60 wt % soft-segment content (PEE15); (c) 80 wt % soft segment content (PEE17); (d) 100 wt % soft segment content (PEE20); Magnification 10,000× (a) or 6000× (b–d); scales shown at the top of the individual micrographs.

cle surface reflects a trend corresponding to the particle volume, which can be evaluated using a correction formula for the so-called "tomato slice problem"[12] necessary for a more precise interpretation of the surface areas. However, the more exact interpretation of the data seems not to be very significant due to the large standard deviations in the measurements of the particle diameters.

In Figure 8(b)–(d), it is also remarkable that a varying number of particles in the samples was torn out, although all samples were prepared with the same diamond knife. The specimen of the resin with 80 wt % ssc in the modifier exhibiting the peak value of toughness has the smallest number of holes. In the sample that was modified with soft segment only [Fig. 7(d)], however, all particles were torn out by the cutting process.

Table III   Statistical Comparison of the Modifier[a] Particles in Figures 8(a)–(d)

Soft[b] (Gew %)	Particle-$\varnothing$[c] (μm)	$\Delta\varnothing$[d] $\pm$ (μm)	F_p/F_g[e] (%)
60	0.27	0.06	2.8
80	0.6	0.17	6.4
95	0.5	0.16	5.4
100	0.65	0.26	7.9

[a] Terephthalate-to-Isophthalate ratio of the polyetherester = 50 : 50.
[b] Soft-segment content of the polyetherester.
[c] Average particle diameter.
[d] Standard deviation thereof.
[e] Ratio between particle area F_p to surface area F_g.

In contrast to the transmission electron micrographs shown in Figure 8, Figure 9 presents the view of the resin surfaces as investigated using the scanning electron microscope. These samples also demonstrate hole structures in the smooth area close to the crack origin. Compared to the TEM results, the results obtained using the SEM reveal that mean hole diameters increase with an increase in the ssc of the polyetherester modifier. In addition, in the SEM micrographs 8(a)–(d), the outer appearance of the holes varies, depending on the soft-segment content. Thus, the circular structures in the resin modified only with soft segments do appear to be severed particles instead of holes. An individual hole in the center of the micrograph in Figure 9(d) indicates that this is not due to the adjustment of the SEM. Holes that are surrounded by deformation rings appear in the samples that were modified with polyetheresters with 60 and 80 wt % ssc respectively [Fig. 9(b)–(c)]. Comparable hole structures that are
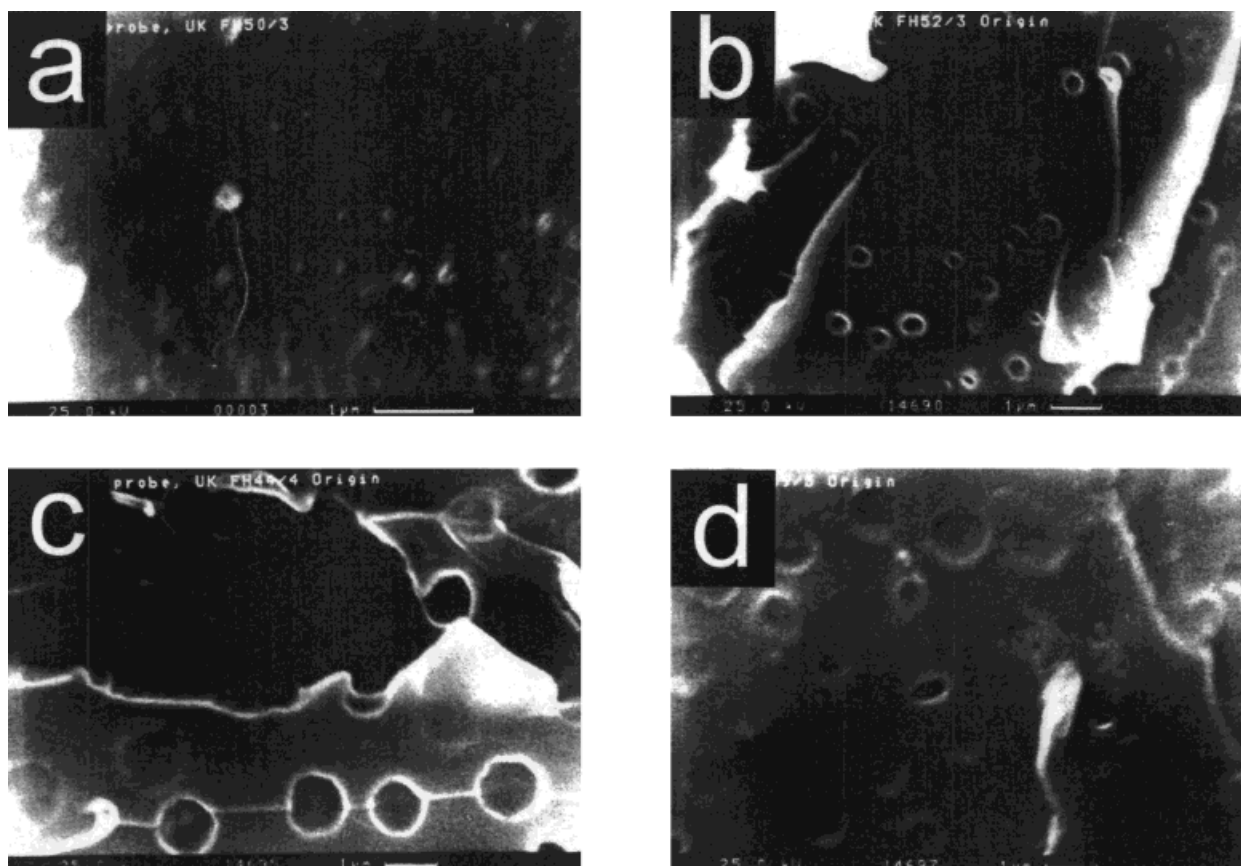

Figure 9   Scanning electron micrographs of fracture surfaces of epoxy/polyetherester (6-GI/T series) blends. (a) 20 wt % soft-segment content (PEE13); (b) 60 wt % soft-segment content (PEE15); (c) 80 wt % soft-segment content (PEE17); (d) 100 wt % soft-segment content (PEE20). Magnification 13,600× (a) or 7225× (b–d); scales shown at the bottom of the individual micrographs.

dependent on the modifier contents can also be observed in the 6-GT modified resins.

DISCUSSION

The solubility of the polyetheresters in the epoxy resins is only partially reflected by the thermal and mechanical behavior of the polyetherester/ epoxy blends. Although polyetheresters with high hard-segment content are soluble in the epoxy resins used, the glass transition temperatures drop only a few degrees. The stiffness of the matrix framework of these resins is hardly disturbed by the soluble polyetherester modifiers, as shown by the elastic moduli, which drop only slightly compared to the unmodified resin. A possible explanation of the negligible plastification of the epoxy matrix is seen in the crystallinity of the hard segments. Robertson[13] also found a very slight drop in the elastic modulus and tensile strength of poly(butylene terephthalate)-modified epoxy resins. Both modifiers, poly(butylene terephthalate) and poly(hexamethylen terephthalate), the latter used in this study as a hard segment, are similar in chemical structure and also have comparable crystallinities.[14]

In general, variations in the hard-to-soft segment ratio in the polyetheresters lead to changes in the mechanical characteristics of the modified epoxy resins. Increasing the soft-segment content in the oligomeric polyetherester modifiers of both series (6-GT and 6-GI/T) results in an increase in the toughness, as revealed in the rise of the K_{Ic} values and the drop in both the tensile strength and the elastic modulus.

In addition to the trends dealing with the dependence on modifier composition, described above, the results of all tensile and toughness tests of both series exhibit a maximum in the area between 60 and 90 wt %. To interpret this behavior, the deformation mechanisms of thermoplastic or elastomeric modifiers in interaction with a brittle matrix must be considered. During tensile loading of the specimen, both stress concentrations at the particle interfaces and dilatation stress in the particles are built up. If the network density of the epoxy resin is not too high, the energy will be reduced mainly by a plastic deformation processes within the matrix.[15–17] According to Pearson,[18,19] in DDS-hardened DGEBA epoxy resin systems this type of energy dissipation also applies for molecular weights between two network points up to 1000 g/mol. This deforma-

tion mechanism was confirmed by SEM photographs for the systems studied here having a network density in a similar range. The white lines that appear in Figure 9(c)–(d) can be classified as plastic shear bands.[20] Accordingly, toughness enhancement should be related primarily to the interfacial area between particle and matrix because shear deformation would be expected to start at this location.[21,22] The competing process, crazing, can be excluded for highly crosslinked thermosets due to a lack in segment mobility, as was shown by different authors.

It can be assumed that the compatibility between the polyetherester and the epoxy resin improves with increasing polyetherester soft-segment content, resulting in an optimal phase adhesion at levels between 70 and 85 wt % ssc. Taking the K_{Ic} values of the 6-GT series resins in Figure 6 and the appropriate data of resins that were modified by the model segments POTM2000 and PHT1000 in Figure 7, it can be noticed that the toughness increase is connected to the block character of the polyetherester. The observed increase in toughness of up to 60% can be attributed to an optimized interfacial adhesion.

Although the optimized toughness can be explained with a phase adhesion model, it is not as simple to account for a synergy between strength and toughness. A second effect must be present that can explain the recovery of strength and modulus in Figures 4 and 5. To do so, the micrographs in Figures 8 and 9 should be inspected more in detail. In addition to the varying particle sizes in the elastic bright field pictures in Figure 8, a varying number of torn out particles can also be discerned. Although all samples were prepared with the same tools, the sample with 80 wt % soft segment, i.e., the maximum of the synergy area, shows the lowest number of torn particles. Apparently, this sample has better cohesion within the particles than samples with other modifier contents. It is also conceivable that this is due to good adhesion between phases, but then it would be expected that polyetheresters with less than 80 wt % soft-segment content would have even fewer torn particles because the tolerability of the block copolymers to the epoxy resin increases with decreasing soft-segment content.

The improvement in cohesion within the modifier could account for the renewed rise in the strength and elastic modulus. It is well-known that discrete modifier particles within a brittle matrix generally contain a certain amount of matrix material.[23,24] In block copolymers containing

a segment that is soluble in the matrix material, there is a strong interaction and, thus, a large amount of matrix material can be expected within the particles. Furthermore, beyond a certain percentage it can be expected that crosslinking occurs, and this results in an increase in cohesion. In this case, it can be inferred that there is a semiinterpenetrating network, because it is unlikely that the polyetherester could still develop a physical network under these conditions. Studies from Sefton[25] and Hsieh[26] show that this model is quite reasonable. These authors studied different thermoplastics such as polyurethanes with regard to their suitability as toughening agents for epoxy resins. They discovered for optimally adjusted compatibility between the thermoplastic modifier and the resin matrix semiinterpenetrating networks be formed, leading to a considerable increase in toughness. Another indication of the strong interaction between the polyetherester with 85 wt % soft-segment content and the epoxy resin was achieved in a study on epoxy resin modified with polyetherester of higher molecular weight.[27] In these systems containing only a 10 wt % modifier phase, an inversion or coexisting phase does appear; this can only be explained assuming a complex blend structure of polyetherester and epoxy resin. On the other hand, the question arises as to why crosslink formation in the particles does not occur in polyetheresters with hard segment contents as low as 50–60 wt %. This could be explained by taking into account the migration of epoxy resin-compatible hard segments to the particle/matrix interface. Combined with the small particle size, this could lead to a small effective concentration of hard segments in the interior of the particle, and subsequently, also to concentrations of epoxy resin within the particles too small for crosslinking.

Furthermore, there must also be differences in the deformation mechanism due to a change in the polyetherester composition, as indicated comparing the scanning electron micrographs of the different epoxy resin blend in Figure 9. The holes in the fracture surfaces in Figure 9(b) and (c) are presumably due to the cavitation of the modifier particles, while on the fracture surfaces in Figure 9(d) the particles in the resin modified by the soft segment only appear to be cut in half by the running crack. The observation that the particles were split is an additional indication for inferior cohesion within the particles compared to the adhesion between particle and matrix.
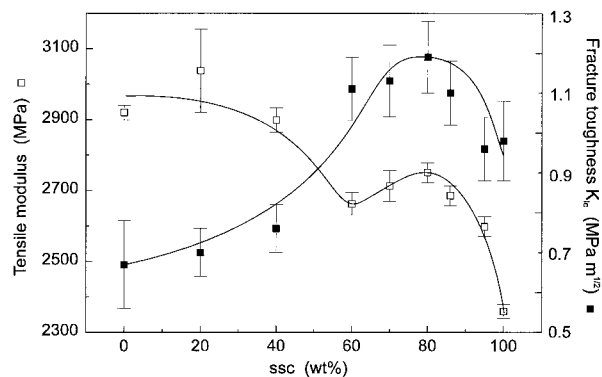

Figure 10 Comparison of tensile modulus ($\square$) and fracture toughness ($\blacksquare$) of epoxy resins modified with 10 wt % polyetherester (6-GT series) as functions of modifier composition (as taken from Figs. 5 and 6).

It can be concluded that epoxy resins modified with relatively small amounts (10 wt %) of polyetherester block copolymers consisting of polyoxytetramethylene soft segments and poly-(hexamethyleneterephtalate) hard segments exhibit mechanical properties strongly depending on polyetherester molecular architecture. Increasing soft-segment content (and, thus, also decreasing hard segment content) of the modifier affects the increasing fracture toughness in combination with the decreasing elastic modulus and tensile strength. However, there is a special composition in the range of about 70–90 wt % soft segments in the polyetherester with a synergetic increase in both toughness and tensile properties. An increase of fracture toughness and elastic modulus (as well as tensile strength) leads to peak values of these properties for the same modifier composition, as shown in Figure 10.

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