

# Use of Hygrothermal Decomposed Polyester–Urethane Waste for the Impact Modification of Epoxy Resins

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**ABSTRACT:** Hygrothermally decomposed polyurethane (HD-PUR) of a polyester type was used as an impact modifier in tri- and tetrafunctional epoxy (EP) resins. Between 5 and 80 wt % of the PUR modifier was added to the EP prior to its crosslinking with a diamine compound (diaminodiphenyl sulfone, DDS). The mean molecular weight between crosslinks ( $M_c$ ) was determined from the rubbery plateau modulus of the dynamic mechanical thermal analysis (DMTA) spectra. The fracture toughness ( $K_{Ic}$ ) and energy ( $G_c$ ) of the modified resins were determined on static-loaded compact tension (CT) specimens at ambient temperature. The change in the  $K_{Ic}$  and  $G_c$  as a function of  $M_c$  followed the prediction of the rubber elasticity theory. The efficiency of the HD-PUR modifier was compared with that of a carboxyl-terminated liquid nitrile rubber (CTBN). Attempts were also made to improve the functionality of the modifier by hygrothermal decomposition of PUR in the presence of glycine and  $\epsilon$ -caprolactam, respectively. DMTA and fractographic results showed that HD-PUR functions as an active diluent and a phase-separating additive at the same time. As HD-PUR can be regarded as an amine-functionalized rubber, it was used as the hardener (by replacing DDS) in some EP formulations. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1139–1151, 2000

**Key words:** epoxy toughening; fracture toughness; hygrothermal decomposition; polyester–urethane; theory of rubber elasticity; toughening mechanisms

## INTRODUCTION

To improve the low inherent toughness of epoxy (EP) resins, various methods have been developed. Incorporation of rigid inorganic (e.g., aluminum oxide, silicon dioxide, barium titanate, dolomite, glass beads, aluminum hydroxide<sup>1–3</sup>) or organic fillers (with<sup>4,5</sup> and without solubility<sup>6,7</sup> in the EP resin) is one of the widely used options. Core–shell-type rubbers with and without functionalization<sup>8–10</sup> may be considered as a subgroup

of the organic fillers, as their mean particle size is well defined although their toughening mechanisms may differ from the thermoplastic powders. Microvoids<sup>11</sup> and even microholes produced via solvent vapor-induced phase separation<sup>12</sup> can also fulfill the role of a toughness modifier. It is widely accepted that the modifier particles, acting as stress concentrators, release the local triaxial stress state by various mechanisms and trigger the shear deformation of the EP network.

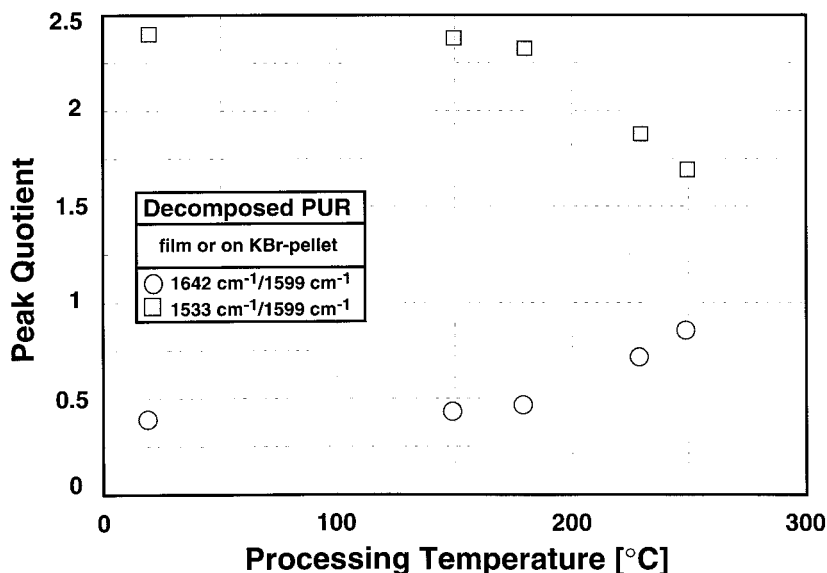
A rather old but very efficient method is to add functionalized liquid rubbers, like carboxyl-, amine-, or epoxy-functionalized nitrile<sup>13–17</sup> or silicon rubbers<sup>18,19</sup> to the crosslinking EP resin. These rubbers are mostly soluble in EP but precipitate in the form of droplets during crosslinking of the EP. The mean size of the droplets depends on several factors such as type, functionality, and amount of the rubber, type of the

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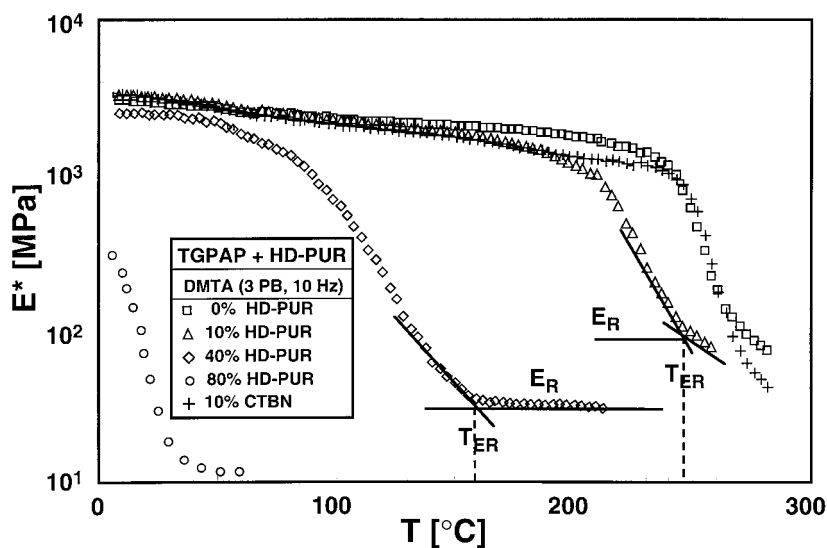


**Figure 1** FTIR results showing the hydrolytical cleavage of urethane bonds.

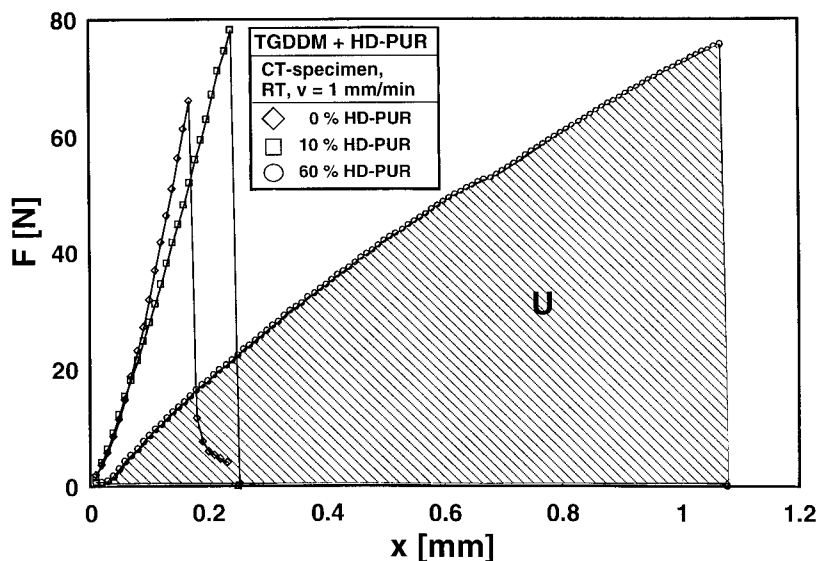
hardener, and crosslinking conditions. The droplets cavitate themselves or induce cavitation of the EP matrix via decohesion (debonding) during loading. This is associated with a change in the stress condition from plane strain toward plane stress, which favors the shear deformation of the EP matrix. The outcome of this failure scenario is improved toughness. It is intuitive that the shear deformability of the EP depends on its crosslink density. Note that functionalized liquid rubbers provide the EP with the highest toughness.

Therefore, it is a great challenge to find a suitable replacement for such rubbers, including liquid nitrile rubbers, which are rather expensive.

Our research philosophy was to use a hygrothermally decomposed polyurethane of a polyester type (HD-PUR) as an impact modifier for EP resins. A further aim of this study was to check how the fracture mechanical parameters of the HD-PUR-modified EP resins depend on the characteristics of the crosslinking structure.<sup>20</sup> In the literature, there are numerous publications stat-



**Figure 2**  $E^*$  versus  $T$  traces for a trifunctional EP with various amounts of HD-PUR. Note: This figure shows the definition of  $E_R$  used to calculate  $M_c$ .



**Figure 3** Load/load-line displacement ( $F - x$ ) plots for a tetrafunctional EP without and with various amounts of HD-PUR

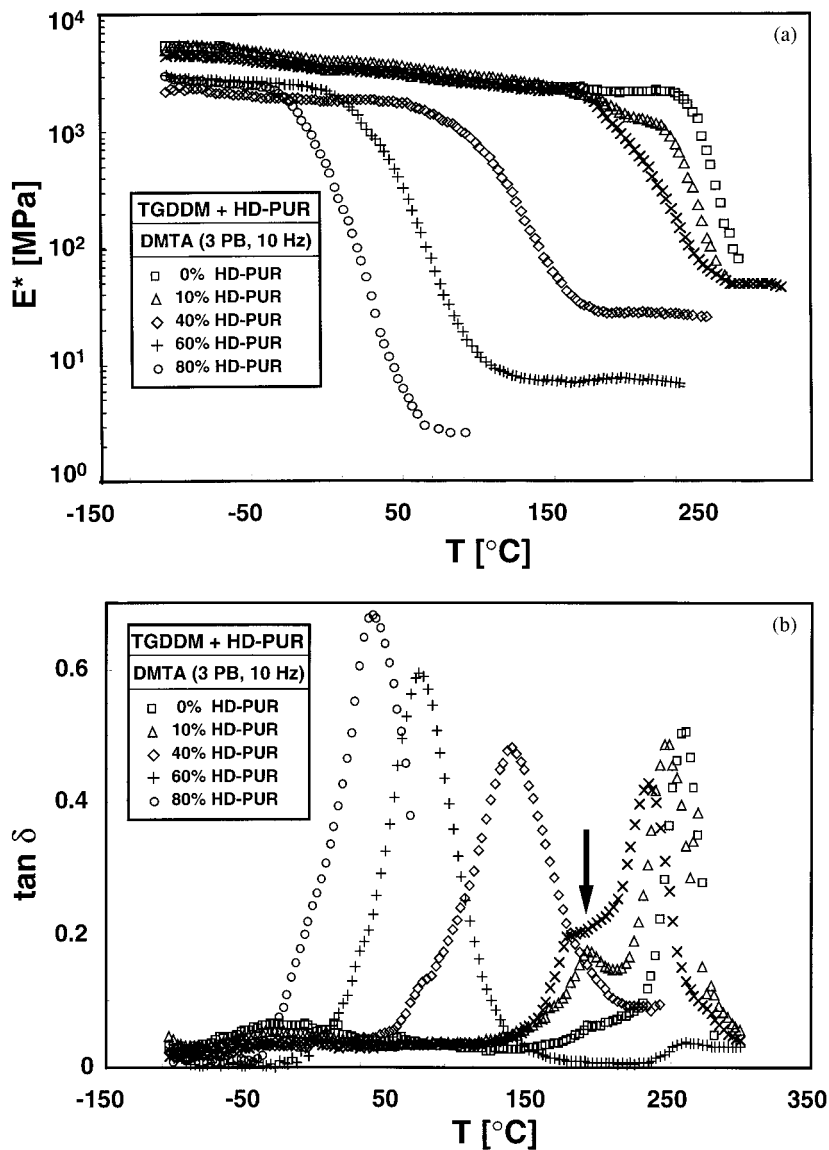
ing that the fracture toughness ( $K_c$ ) and energy ( $G_c$ ), as a function of crosslinked network parameters, can be described by the rubber elasticity theory. Accordingly,  $K_c$  and  $G_c$  change as a function of the mean molecular weight between crosslinks ( $M_c$ ) by linear and square-root relations, respectively.<sup>21-24</sup> Another aim of this work was to check whether the efficiency of HD-PUR can be improved by performing partial hygrothermal decomposition in the presence of suitable co-agents.

## EXPERIMENTAL

### HD-PUR and Its Characteristics

Polyester-based PUR processing waste from the footwear industry was ground in an air-cooled cutting mill to a particle size of 1–3 mm. To the PUR particles, 10 wt % of water (sometimes as a solution with co-agents—see below) was added and fed in the hopper of a laboratory-scale twin-screw extruder. The extruder was heated to temperatures from 150 to 250°C, depending on the required decomposition degree. The hygrothermally decomposed product was a more or less kneadable paste. HD-PUR, which was extruded at 150°C, looks rather like the virgin material, whereas the product produced at 250°C is a soft and sticky paste, even at ambient temperature.

The decomposed PUR was characterized by three different methods: The viscosity, which decreases with increasing decomposition degree, was measured by plate/plate rheometry at 170°C. The reason for the selection of this rather high temperature is that the original PUR and the HD-PUR of a lower decomposition degree are not “soft” enough at lower temperatures, so their viscosity could not be determined. The degree of decrosslinking, and, respectively, the residual crosslinking density, was determined by acetone-soluble and -insoluble fractions. For the extraction (4 h), a Soxhlet apparatus was used. With increasing progress of the hydrolytic decomposition, the acetone-insoluble residue of HD-PUR became smaller and smaller. The hydrolytic cleavage of the urethane bonds reduced the amount of secondary amines and increased that of the primary amines. This was detected by Fourier transform infrared spectroscopy (FTIR). The peak heights at wavenumbers of 1533 and 1642  $\text{cm}^{-1}$  divided by the peak height at 1599  $\text{cm}^{-1}$  as a function of the extrusion temperature are given in Figure 1. Recall that the peaks at 1533 and 1642  $\text{cm}^{-1}$  are assigned to secondary and primary amines, whereas the peak at 1599  $\text{cm}^{-1}$  refers to aromatic carbon-carbon double bonds and thus may serve as a reference peak.<sup>25</sup> The HD-PUR used in this study was extruded at 230°C and exhibited a melt viscosity of  $0.9 \times 10^3$  Pa s at 170°C. Its acetone-insoluble fraction was 14 wt %.



**Figure 4** (a)  $E^*$  versus  $T$  traces for a tetrafunctional EP with various amounts of HD-PUR. (b)  $\tan \delta$  versus  $T$  traces for a tetrafunctional EP with various amount of HD-PUR.

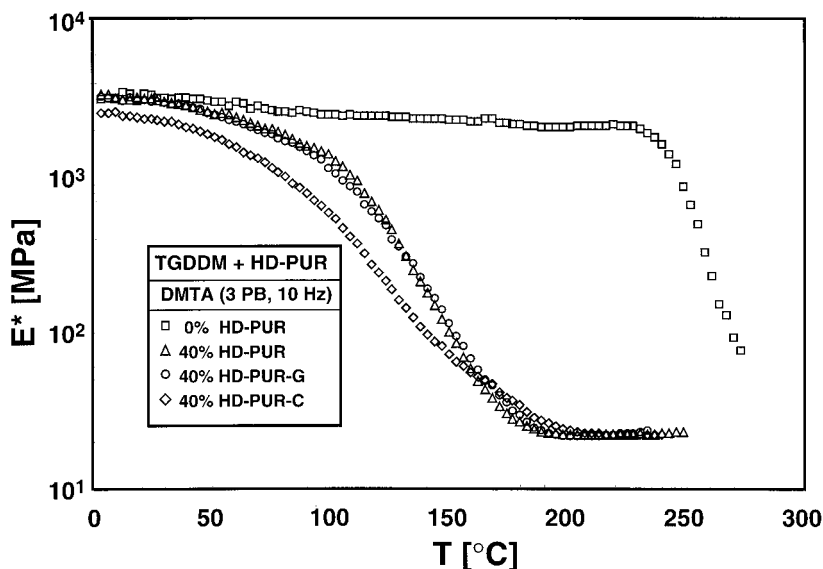
The original, untreated PUR had an 87 wt % acetone-insoluble residue and  $15 \times 10^3$  Pa s viscosity.

Although the HD-PUR already contains some functional groups, especially amino groups (cf. Fig. 1), attempts were made to increase its functionality by using bifunctional additives during the hydrothermal decomposition process. It is known that compounds either with carboxyl or amino groups are able to break up the crosslinked structure of PUR,<sup>26</sup> so the addition of substances containing both functional groups should increase the functionality of the decomposed PUR. Two

substances (coagents) were chosen for that purpose: glycine (G) and  $\epsilon$ -caprolactam (C). The coagent (5 wt %) was diluted with water and added to the PUR particles during the extrusion decomposition as described above. The viscosity and acetone residue of the related products were  $0.1 \times 10^3$  Pa s and 34 wt % (HD-PUR-G) and  $0.4 \times 10^3$  Pa s and 13 wt % (HD-PUR-C).

#### Modification of the EP Resins

Two types of EP resins were used: a tetrafunctional [tetraglycidyl diaminodiphenyl-methane



**Figure 5**  $E^*$  versus  $T$  traces for a tetrafunctional EP without and with 40 wt % HD-PUR produced in the presence of various coagents.

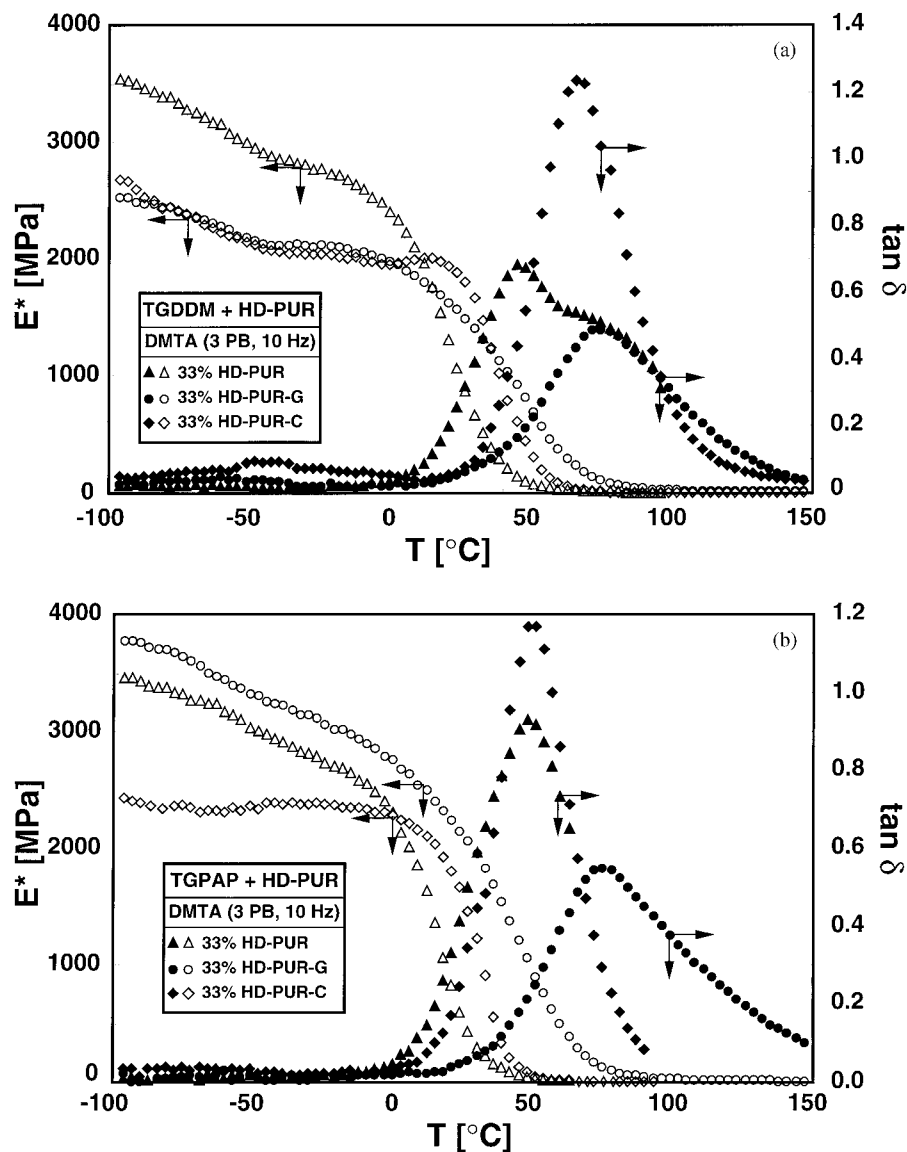
(TGDDM), Araldite MY 720, Ciba, Basel, Switzerland] and a trifunctional [triglycidyl-*p*-aminophenol (TGPAP), MY 0500, Ciba] resin. Due to the very high viscosity of MY 720 at room temperature (RT), the resin was warmed to 50°C before use. HD-PUR was mixed with the EP in a broad composition range (from 5 to 80 wt %). The EP/HD-PUR mixture was homogenized by stirring before the hardener, diaminodiphenyl sulfone (DDS; HT 976, Ciba), was introduced and mixed again carefully. The ratio of the EP and the hardener was constant (67 : 33 wt %) in each formulation. Accordingly, the HD-PUR was considered as a neutral filler. This is at odds with the amine functionality of HD-PUR, which, however, has not yet been determined (all our attempts by titration have failed so far). The resin mixtures were then poured into paper beakers and degassed *in vacuo* at 50°C (30 min). After that, the mixture was kept in an oven at 80°C for 30 min and for a further 30 min at 100°C. Subsequently, the modified resin was poured into preheated polytetrafluoroethylene (PTFE) molds. The viscosity of the neat resin is low at  $T = 100^\circ\text{C}$ , but increases with increasing HD-PUR content, so the mixture with 80 wt % HD-PUR is of very poor flowability. Curing of the plaques of 4-mm thickness proceeded by storing the open molds at 120°C for 90 min and finally at 177°C for 120 min. To compare the efficiency of this novel toughening method with the state of the art, an EP modified with 10 wt % of a liquid nitrile rubber (carboxyl-

terminated acrylonitrile butadiene; CTBN, 1300  $\times$  8, BF Goodrich, Oevel, Belgium) was produced in the same way. HD-PUR-G and -C were incorporated into selected EP formulations for the sake of comparison. In a further test series, the DDS was fully replaced by HD-PUR (i.e., added in 33 wt %) and the related resins cured as mentioned above.

#### Characterization of the Toughened EP Resins

Information on the phase structure of the toughened EPs was derived from dynamic mechanical thermal analysis (DMTA). DMTA spectra were taken by using rectangular specimens (50  $\times$  10  $\times$  4 mm<sup>3</sup>; length  $\times$  width  $\times$  thickness) in the flexural mode at 10 Hz using an Eplexor 150 N device of Gabo (Ahlden, Germany). The static and cyclic (sinusoidal) loading components were set for 2 and 1 N, respectively. DMTA spectra, namely, the complex modulus ( $E^*$ ) and its constituents ( $E'$  and  $E''$ ) and the mechanical loss factor ( $\tan \delta$ ) as a function of temperature ( $T$ ), were measured in the interval  $T = -100$  to  $+300^\circ\text{C}$  at a heating rate of 0.6°C/min.

The apparent mean molecular weight between crosslinks ( $M_c$ ) was computed by considering the rubbery plateau just above the glass transition ( $T_g$ ), which could be well resolved for EPs with a high amount of HD-PUR (cf. Fig. 2). For the EPs with less HD-PUR, the onset of the plateau modulus was taken (determined as indicated in Fig.



**Figure 6** (a)  $E^*$  versus  $T$  and related  $\tan \delta$  versus  $T$  traces for a tetrafunctional EP resin cured by “functionalized” HD-PUR without additional DDS. Note: HD-PUR content is 33 wt %. (b)  $E^*$  versus  $T$  and related  $\tan \delta$  versus  $T$  traces for a trifunctional EP resin cured by “functionalized” HD-PUR without additional DDS. Note: HD-PUR content is 33 wt %.

2), as for these formulations the  $T_g$  and the thermal decomposition temperature were closely matched.  $M_c$  was calculated by the basic equation of rubber elasticity:  $E_R = 3nRT = 3(d/M_c)RT$ , where  $E_R$  is the rubbery plateau modulus (as defined in Fig. 2);  $d$ , the density of the resin;  $R$ , the universal gas constant; and  $T$ , the plateau onset temperature  $T_{ER}$  (cf. Fig. 2).<sup>27</sup>

#### Fracture Mechanical Parameters

The determination of fracture toughness ( $K_c$ ) and fracture energy ( $G_c$ ) was done in accordance with

the ESIS testing protocol from 1996.<sup>28</sup> The tests were done with a Zwick universal testing machine type 1445. The notch of the compact tension (CT) specimens (dimension:  $35 \times 35 \times 4$  mm<sup>3</sup>), sawed from the cured plates, was sharpened by a razor-blade prior to their tensile loading at RT with a crosshead speed of  $v = 1$  mm/min. For the  $K_c$  determination, the maximum load ( $F_{max}$ ) of the CT specimens was always considered:

$$K_c = f \frac{F_{max}}{BW^{1/2}}$$



**Table I** Experimental  $E_R$ , the  $T_{ER}$ , and  $M_c$ ,  $K_c$ , and  $G_c$  Values

Composition (wt %)	$E_R$ (MPa)	$T_{ER}$ (°C)	$M_c$ (g/mol)	$K_c$ (MPa m <sup>1/2</sup> )	$G_c$ (kJ/m <sup>2</sup> )	
TGDDM + DDS (33 wt %)						
+ HD-PUR	0	76.7	273	228	0.53	0.23
	5	70.3	268	245	1.00	0.64
	10	40.1	265	429	0.90	0.49
	20	65.9	252	254	0.81	0.47
	40	37.5	163	366	1.21	0.79
	60	7.9	126	1561	0.96	1.79
	80	2.9	63	3251	—	—
+HD-PUR-G						
	5	31.2	272	559	0.80	0.38
	10	30.4	270	564	0.83	0.49
	20	38.4	250	435	0.80	0.39
	40	29.4	180	490	1.19	0.92
+HD-PUR-C						
	5	68.1	269	255	0.99	0.63
	10	34.6	241	476	1.08	0.76
	40	28.1	185	519	1.15	1.01
TGDDM + HD-PUR						
+ HD-PUR-G	33	15.3	57	615	—	—
+ HD-PUR-C	33	23.7	100	456	1.1	0.65
TGPAP + DDS (33 wt %)						
+ HD-PUR	0	104.4	267	173	0.61	0.25
	5	98.3	262	179	0.61	0.27
	10	101.2	256	171	0.98	0.62
	20	111.3	222	145	0.71	0.35
	40	43.8	150	309	1.66	1.54
	60	11.0	115	1114	1.35	3.15
	80	8.4	33	1067	—	—
+HD-PUR-G						
	5	100.5	258	174	0.90	0.50
	10	114.5	247	149	0.94	0.54
	20	79.2	223	205	1.07	0.80
	40	27.6	159	506	1.41	1.10
+HD-PUR-C						
	5	112.4	261	156	0.86	0.49
	10	121.8	256	142	0.97	0.65
	40	33.1	147	410	1.41	1.22
TGPAP + HD-PUR						
+HD-PUR-G	33	12.5	50	749	—	—
+HD-PUR-C	33	20.9	102	537	1.2	0.70
	33	5.3	69	1923	—	—

where  $f$  is the calibration factor;  $B$ , the thickness; and  $W$ , the specimen width.  $f$  is given by

$$f = \frac{(2 + \alpha)}{(1 - \alpha^2)} [0.886 + 4.64\alpha - 13.32\alpha^2 + 14.72\alpha^3 - 5.6\alpha^4]$$

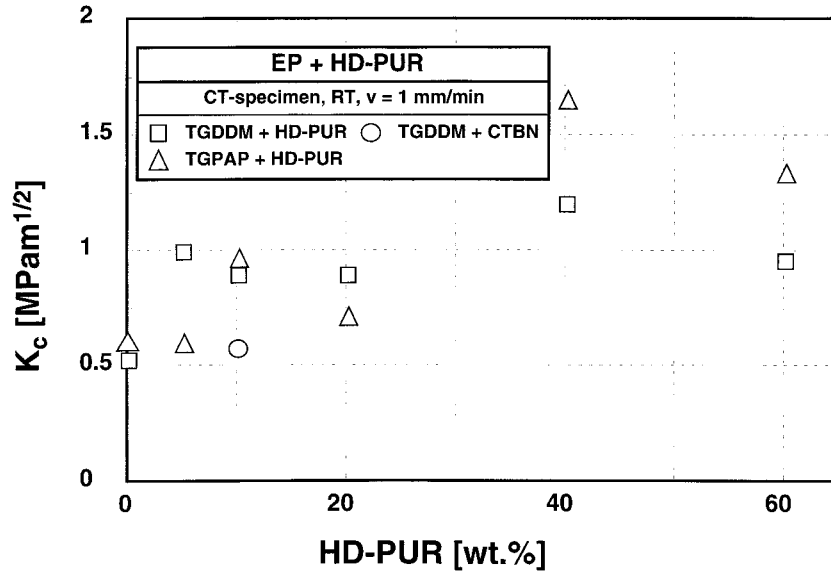
where  $\alpha = a/W$ , and  $a$ , the overall notch length.

The load/load-line displacement ( $F - x$ ) plots shown in Figure 3 make clear that the approach of linear elastic fracture mechanics (LEFM) can be well applied for these materials.  $G_c$  was calculated by the equation

$$G_c = \frac{U}{BW\phi}$$

where  $U$  is the energy up to  $F_{max}$  (read from the  $F - x$  plot; cf. Fig. 3), and  $\phi$ , the energy calibration factor. For CT specimens,  $\phi$  is

$$\phi = \frac{(1.9118 + 19.118\alpha - 2.5122\alpha^2 - 23.226\alpha^3 + 20.54\alpha^4)(1-\alpha)}{(19.118 - 5.0244\alpha - 69.678\alpha^2 + 82.16\alpha^3) \times (1-\alpha) + 2(1.9118\alpha - 2.5122\alpha^2 - 23.226\alpha^3 + 20.54\alpha^4)}$$



**Figure 7**  $K_c$  versus HD-PUR content for tri- and tetrafunctional EP resins with DDS hardener. Note: This figure also contains the result achieved by adding 10 wt % CTBN rubber.

### Fractography

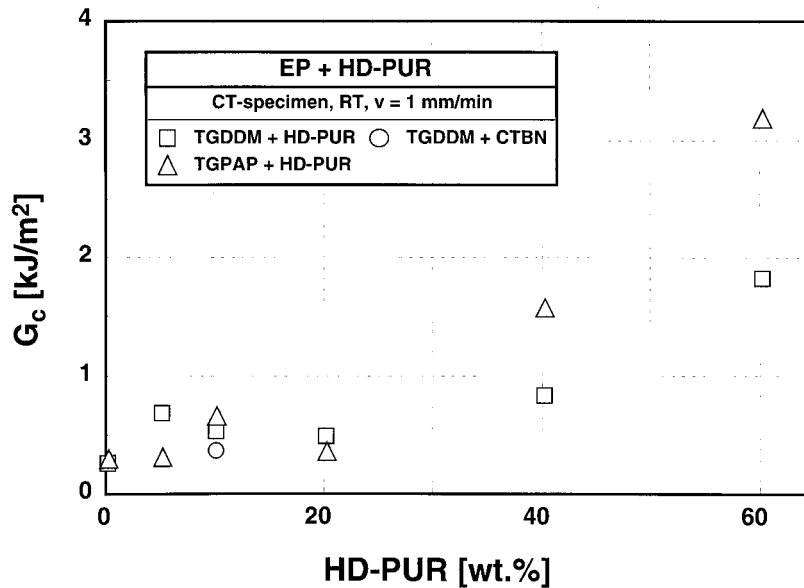
The fracture surfaces of some selected compact tension specimens were coated with an alloy of Au/Pd and examined in a scanning electron microscope (SEM; JSM-5400, JEOL, Tokyo, Japan). SEM inspection was focused on the vicinity of the razor notch which reflects the initiation failure mode. Some fracture surfaces were also examined by atomic force microscopy (AFM, Digital Instru-

ments) in the tapping mode. AFM proved to be a useful tool to study the phase structure and failure mode in modified EPs.<sup>29</sup>

## RESULTS AND DISCUSSION

### Network Structure and Its Characteristics

Figure 2 shows the  $E^*$  versus  $T$  traces for the trifunctional EP modified by various amounts of



**Figure 8**  $G_c$  versus HD-PUR content for tri- and tetrafunctional EP resins with DDS hardener. See note in Figure 7.



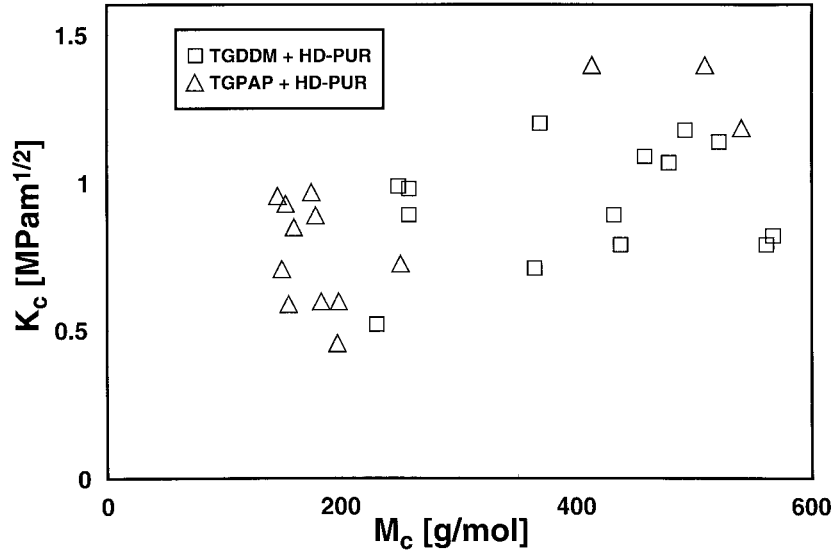


Figure 9  $K_c$  plotted against  $M_c$  for the tri- and tetrafunctional EPs studied.

HD-PUR and for the same resin modified with 10 wt % CTBN. One can see that, with an increasing amount of the modifier, the  $T_g$  shifts toward lower temperatures. Further, the  $T_g$  decrease for the HD-PUR-modified EP resin is greater than for the CTBN-modified material at the same modifier content. Parallel to this change, the  $E_R$  values decreased, which means an increment in the related  $M_c$  data. At higher HD-PUR content, the rubbery plateau became clearly discernible (being no more affected by the thermal decomposition).

The reduction in both  $T_g$  and  $E_R$  implies that the HD-PUR participated in the crosslinking reaction and, thus, in the formation of the crosslinked network structure. As a consequence, HD-PUR works as an active diluent (plasticizer) in EP. This is corroborated also by the stiffness decrease of the EP compounds. Note that the  $E^*$  versus  $T$  curves in Figure 2 shift toward lower stiffness values with increasing modifier content (which, by the way, is also the case with the CTBN-modified resin but without a considerable  $T_g$  shift).

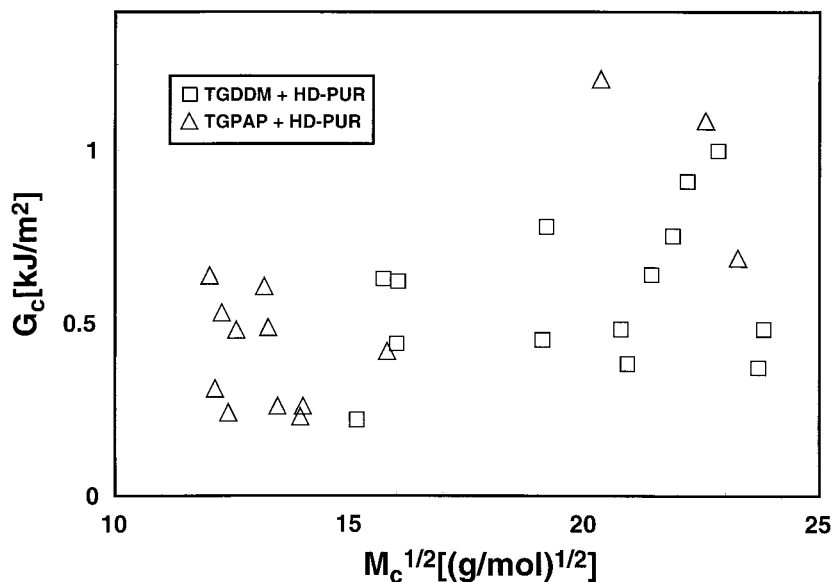
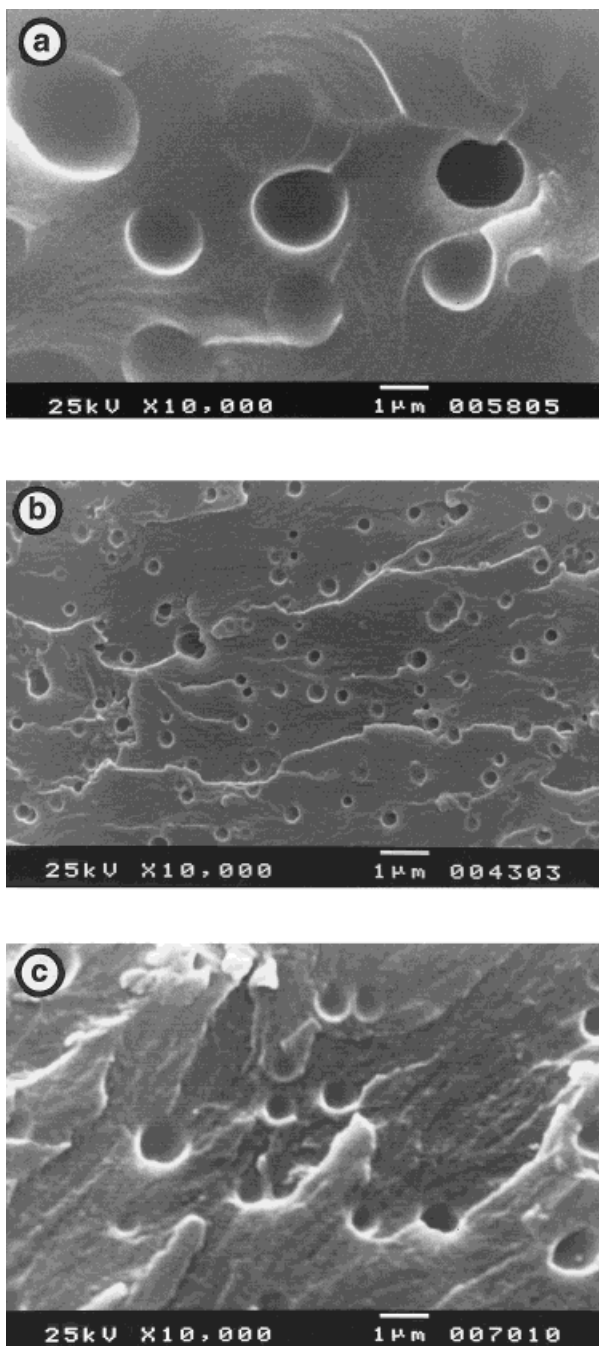


Figure 10  $G_c$  versus  $M_c^{1/2}$  for the tri- and tetrafunctional EPs studied.

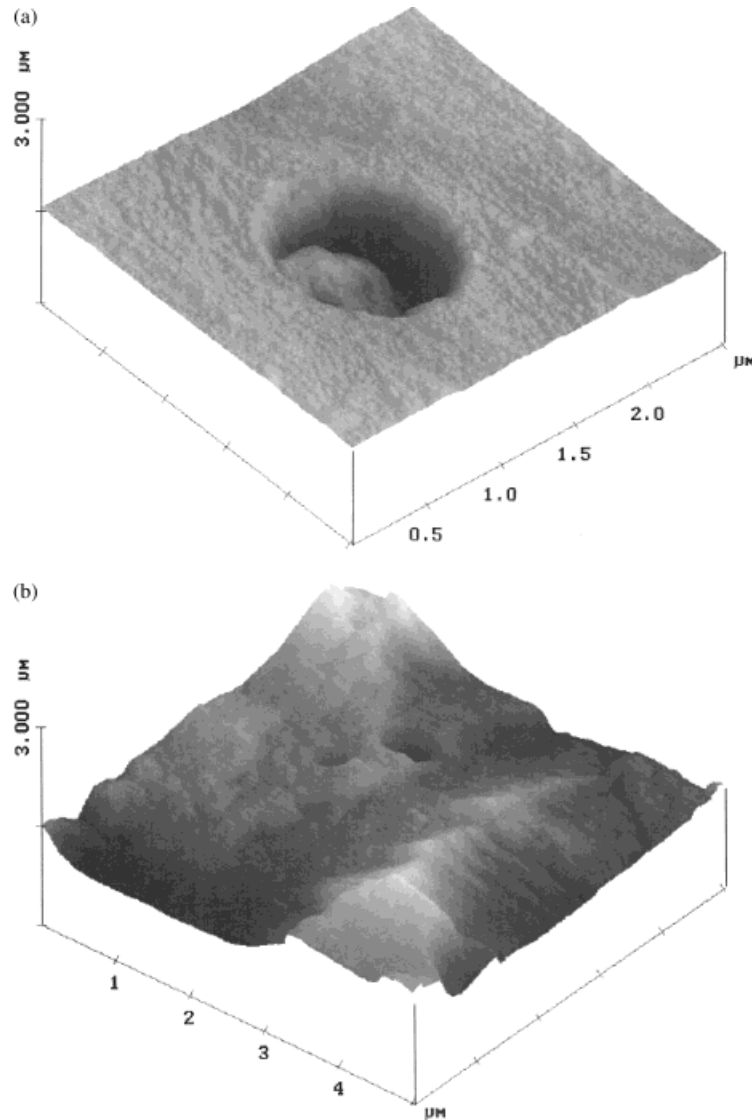


**Figure 11** SEM pictures taken on the fracture surface of toughened EP compounds: (a) 10 wt % CTBN modifier; (b) 10 wt % HD-PUR; (c) 60 wt % HD-PUR.

Figure 4 compares the DMTA response of the HD-PUR-toughened tetrafunctional TGDDM resin. Again, Figure 4(a) demonstrates that HD-PUR acts as a reactive plasticizer in the EP resin. The  $\tan \delta$  versus  $T$  traces in Figure 4(b) are even more informative. Attention should be paid to the

appearance of a shoulder on the  $T_g$  peak [arrow indicates in Fig. 4(b)] at low HD-PUR concentrations and to its changes at higher HD-PUR content. As long as the  $T_g$  peak of the EP resin is not affected by the modifier, the modifier should undergo a complete phase separation during cure. This was demonstrated by the example of EPs toughened by amine-terminated polyoxypropylene recently.<sup>30</sup> The shift in the shoulder toward lower temperatures, and the fact that it becomes a single  $T_g$  peak at high HD-PUR concentrations, suggests, however, the reactive plasticification role of HD-PUR. As this  $T_g$  peak is rather broad, one can assume that the HD-PUR is involved in the formation of both the crosslinked EP network and the disperse phase. Note that the phase separation should be favored by the residual crosslinking degree of the HD-PUR. According to the  $\tan \delta$ - $T$  traces in Figure 4(b), at low HD-PUR content, phase separation should also occur. The above findings are not particularly surprising as the hydrolytic decomposition of PUR resulted in a primary amine-rich rubbery compound. Note that such compounds are often used to toughen EP.<sup>14,15,30</sup> Looking at the DMTA results of the EPs modified with “functionalized” HD-PUR (i.e., HD-PUR-G or HD-PUR-C; cf. Fig. 5), the same trend can be deduced:  $E^*$  and  $T_g$  are decreased by adding HD-PUR of a higher amine functionality.

The DMTA response after replacing the DDS hardener with the same amount of HD-PUR is given in Figure 6 for both the TGDDM and TG-PAP systems. Interestingly, a cured EP still can be obtained when the DDS is fully replaced by HD-PUR. Notice, however, that by adding HD-PUR as a hardener a system of very low  $T_g$  can be produced. Nevertheless, this is experimental proof for the functionality (amine type) of HD-PUR. This is also supported by the fact that the  $T_g$  of the cured resin increases when glycine-modified HD-PUR (HD-PUR-G) is used. This HD-PUR-G should have a higher (amine) functionality and, therefore, a higher potential to participate in the crosslinking reactions. Considering the fact that an analogous shift in the  $T_g$  of EP, as shown in Figure 6, can be produced at a nonstoichiometric ratio (viz., reduced hardener/resin ratio), this may help us to estimate the average functionality of HD-PUR. Table I lists the experimental  $E_R$ , the  $T_{ER}$ , and the calculated  $M_c$  values for the compositions studied.



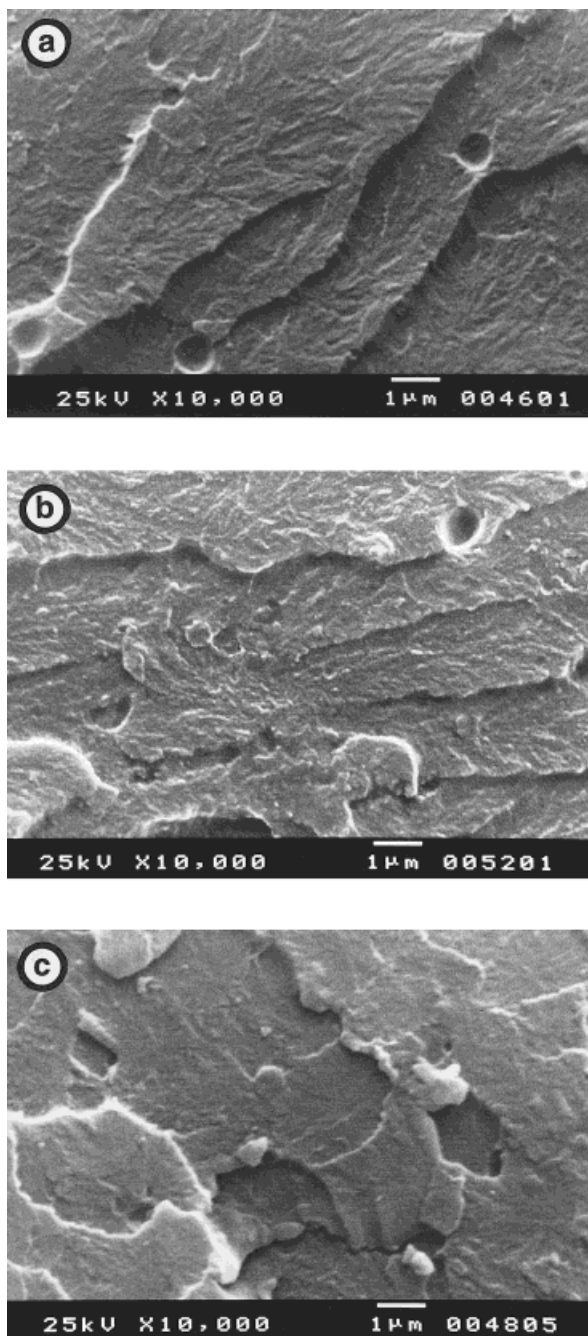
**Figure 12** AFM pictures taken on the fracture surface of toughened EP compounds: (a) 20 wt % HD-PUR; (b) 60 wt % HD-PUR.

#### Fracture Mechanical Data and Their Relation with the Network Parameter $M_c$

Figures 7 and 8 depict the  $K_c$  and  $G_c$  data as a function of the HD-PUR content. One can notice that the fracture toughness is doubled by incorporating as little as 5 wt % HD-PUR. On the other hand,  $K_c$  seems to go through a maximum as a function of the modifier amount. The course of the  $G_c$  versus HD-PUR content differs from the  $K_c$  response. This is because  $G_c$  is affected also by the stiffness. Note that, under plane stress conditions,  $G_c = K_c^2/E$  holds and  $E$  decreases with increasing HD-PUR content (cf. Figs. 7 and 8). The  $K_c$  and  $G_c$  values of the EP/HD-PUR system with-

out DDS were also determined. TGDDM with 33 wt % HD-PUR-G resulted in  $K_c = 1.1 \text{ MPa m}^{1/2}$  and  $G_c = 0.65 \text{ kJ/m}^2$ . Note that these values are matched with that of the EP containing 40 wt % HD-PUR and DDS.

Provided that the rubber elasticity theory can be adopted for our systems, a linear regression is expected when  $K_c$  is plotted against  $M_c$ . This is the tendency, as shown in Figure 9. The scatter in this figure, and especially the deviation from the linearity at low  $M_c$  values, is believed to be an effect of the ambiguity with the  $M_c$  determination used. Remember that  $E_R$  is usually read from the DMTA spectra at  $T_g + 30\text{--}50^\circ\text{C}$  instead of our



**Figure 13** SEM pictures taken on the fracture surface of toughened EP compounds: (a) 40 wt % HD-PUR; (b) 40 wt % HD-PUR-G; (c) 40 wt % HD-PUR-C.

procedure outlined in Figure 2 (i.e., onset of the rubbery plateau). A further reason is that no parallel DMTA measurements were performed on each EP compound.

Following the above analogy with rubber elasticity, the  $G_c$  versus the  $M_c^{1/2}$  data pairs should also show a linear dependence. This tendency is

also confirmed (Fig. 10). Note that the basic assumption behind the above treatise is that the HD-PUR is built-in chemically in the network without any curing-induced phase separation. The latter effects may cause some further uncertainties in respect to the  $M_c$  values, although this is often disregarded.<sup>27</sup> Remember that the question with the anticipated phase separation in HD-PUR-modified EP is not yet corroborated.

### Fractography

Figure 11 compares SEM pictures taken on the fracture surface of modified TGDDM resins. These SEM pictures represent the fracture at crack initiation as they were taken just behind the razor blade notch. The droplets formed by adding CTBN (10 wt %) are well resolved in Figure 11(a). Figure 11(a) also indicates rubber cavitation and crack pinning mechanisms. Phase separation took place also when HD-PUR was used as a modifier in the same amount [10 wt %; Fig. 11(b)]. This SEM picture also shows the enhanced shear deformation of the EP matrix owing to the modification. It is obvious that the CTBN is present in a coarser dispersion (particle size of about 2  $\mu\text{m}$ ) than is the HD-PUR (mean particle size of ca. 0.3  $\mu\text{m}$ ). This resulted also in improved transparency of the PUR-modified material. On the other hand, the fracture surface of the EP system with 60 wt % HD-PUR shows much fewer cavitated holes than expected based on the HD-PUR content [Fig. 11(c)]. In addition to this, the matrix between the holes appears highly deformed. This is further evidence that the HD-PUR is strongly involved in the network formation and acts as an active plasticizer. The fracture surfaces in Figure 11(b,c) also suggest that the basic toughening events and their sequence are likely to be the same for HD-PUR as known for functionalized liquid rubbers (i.e., cavitation followed by shear yielding of the EP matrix). For clarifying the toughening mechanism, especially the onset of cavitation, AFM pictures can be taken into account. Figure 12(a) shows an AFM picture of the fracture surface of a TGDDM compound with 20 wt % HD-PUR. At the bottom of the hole, the rest of a cavitated HD-PUR particle can be resolved. This was formed when the cavitated HD-PUR droplet was stretched and fractured during loading. On the other hand, the strongly deformed matrix between the holes can be regarded as proof of shear yielding. This latter effect becomes much clearer when an EP tough-



ened by 60 wt % HD-PUR is examined [Fig. 12(b)]. How do the coagents (glycine or  $\epsilon$ -caprolactam) affect the appearance of the fracture surfaces of HD-PUR-modified EP? Figure 13 compares three TGDDM compounds, with 40 wt % HD-PUR, produced with and without different coagents. All fracture surfaces show signs of enhanced matrix ductility. The main difference is the smaller number of holes when a coagent was used. This is likely a consequence of the higher solubility of the "functionalized" HD-PUR in the EP matrix.

## CONCLUSIONS

It was shown in this study that HD-PUR waste may be an efficient toughener for EP. According to our invention,<sup>31</sup> this HD-PUR modifier is involved both in the crosslinking (active plasticizer) and phase-segregation process (formation of micron- and submicron-sized droplets), ensuring high toughness of the related thermoset matrix. The toughness of the novel modifier is comparable with that of state-of-the-art liquid rubber modifiers at low concentrations ( $\leq 10$  wt %). The fracture toughness ( $K_c$ ) and energy ( $G_c$ ) of the EP resins modified by HD-PUR as a function of the mean molecular weight between crosslinks ( $M_c$ ) follows the predictions of the rubber elasticity theory fairly well. The failure mode of the HD-PUR-toughened EP is similar to those containing functionalized liquid rubbers although HD-PUR is not only a phase separating additive but also an active plasticizer at the same time.

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