Modification of Epoxy Resin with α,ω-Oligo(butylmethacrylate)diols

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ABSTRACT: Novel liquid rubbers based on bishydroxy-terminated oligo(butylmethacrylate) were used to toughen anhydride-cured epoxy resins. Concentration and molecular weight of the toughening agents were varied in order to examine the effects on important mechanical properties, such as toughness, strength, stiffness, and glass transition temperature. Experimental data show that telechelic methacrylates are suitable toughening agents for epoxies. The compatibility between resin and toughener can be adjusted by varying the molecular weight of the rubber. The best results are obtained by modifying an epoxy resin with 10 wt% of bishydroxy-terminated oligo(butylmethacrylate) of a molecular weight of 5000 g/mol. Fracture toughness K_{Ic} increases by 150% accompanied by a decrease in modulus of only 11% and in strength of 16%, as compared to the corresponding properties of the neat resin. Due to an almost complete phase separation of the rubber upon curing, the glass transition temperature is scarcely affected. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 785–796, 1998

Key words: liquid rubber; α,ω-oligo(butylmethacrylate)diol; mechanical properties; toughening; epoxy resins

INTRODUCTION

Epoxy resins are highly crosslinked thermosets, which are widely used in different fields of application. They exhibit high strength, stiffness, and temperature resistance. However, due to the inherent brittleness of the network, their use is limited, especially for structural applications. A common approach for toughening plastics is the incorporation of a rubbery phase into the matrix.[1] Rubber toughening of epoxies is based on separation of the rubber phase upon curing, leading to discrete rubbery microspheres within the resin matrix. This morphology enables different energy dissipating mechanisms to take place, for example, local shear yielding of the matrix[2,3] and cavitation of rubber particles,[4] effectively enlarging the fracture energy and, hence also, crack propagation resistance.

The general requirement concerning the modification of plastics for structural applications is that none of the properties toughness, strength, stiffness, and temperature behavior is deteriorated by enhancing another property.

The most commonly used toughening agent for epoxies is carboxyl-terminated butadiene-acrylonitrile-copolymer (CTBN).[5] CTBN-modified epoxy resins exhibit increased toughness but show significantly lower stiffness and strength compared to the neat resin.[6] Another disadvantage of CTBN toughening is the low stability against oxidation due to the high amount of unsaturated bonds in
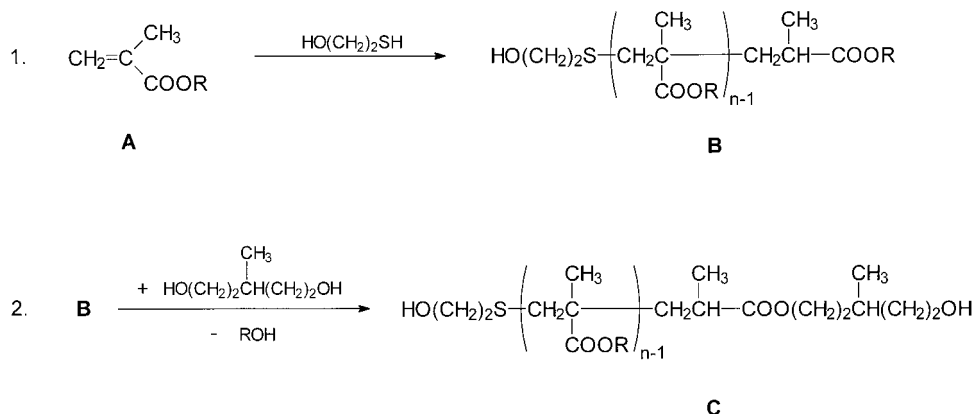
Figure 1 Synthetic strategy to prepare α,ω-oligo(methacrylate)diols.

the CTBN backbone, deteriorating chemical and physical properties of the resin, especially at elevated temperatures.[7] In contrast to CTBN, liquid rubber modifiers based on functionalized acrylic oligomers do not contain unsaturated bonds in the backbone, resulting in good resistance against oxidation processes. This class of materials was used for the toughening of epoxies by Bell et. al.[8–12]

The present study takes up the idea of toughening epoxy resins with oligomeric acrylics. Novel families of α,ω-dihydroxy-terminated oligo(methacrylates) were prepared by Fock et al.[13] according to the synthetic strategy displayed in Figure 1. In a first step, methacrylates (A) are polymerized in the presence of 2-thioethanol in order to prepare hydroxyethylthioether-terminated oligo(methacrylate) (B). In a second step, the ester end group, which is much more reactive with respect to the sterically hindered ester side chains, is transesterified with 3-methylpentanediol yielding dihydroxy-terminated oligo(methacrylates) (C).

MATERIALS

In this investigation, the liquid epoxy resin Araldite GY 250, which is a diglycidylether of bisphenol-A (DGEBA), was cured using hexahydrophthalic anhydride (HHPA) HT 907 in combination with the accelerator N,N-dimethylbenzylamine (DBA) DY 062, all supplied by Ciba-Geigy, Basel (Switzerland).

Several different modifiers based on α,ω-oligo(n-butylmethacrylate)diol, abbreviated as BD, were synthesized. The chemical structure of BD is

shown in Figure 2. The basic materials with molecular weights of 1000 (BD1) and 2000 g/mol (BD2), respectively, were supplied by Th. Goldschmidt AG, Essen, as 25 to 30 wt% acetone solutions. In order to purify the technical rubber solutions from residues of transesterification diol, the solvent was completely removed. The remaining sticky residue was solved in toluene, washed several times with water, and dried using Na_2CO_3. After removing the toluene, the rubber was vacuum-dried at 120°C for 24 h. Subsequently, the materials were redissolved in a defined amount of dry acetone to lower viscosity and therefore facilitate handling.

In order to vary the molecular weight of BD, chain extension was performed by a hexametylenediisocyanate-mediated urethane coupling (Fig. 3). A defined amount of acetone solution of BD2 was mixed with an appropriate molarous amount of hexamethylenediisocyanate (D) in or-
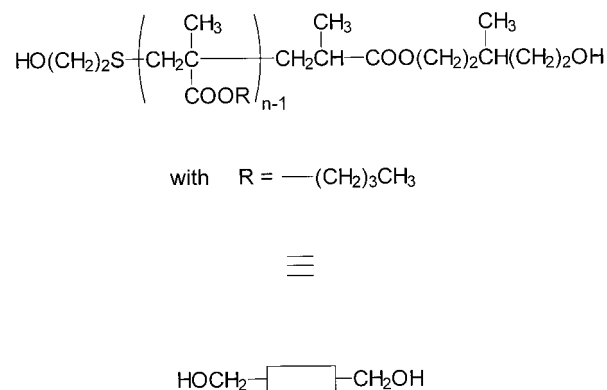

Figure 2 Schematic representation of α,ω-oligo(butylmethacrylate)diol (BD).
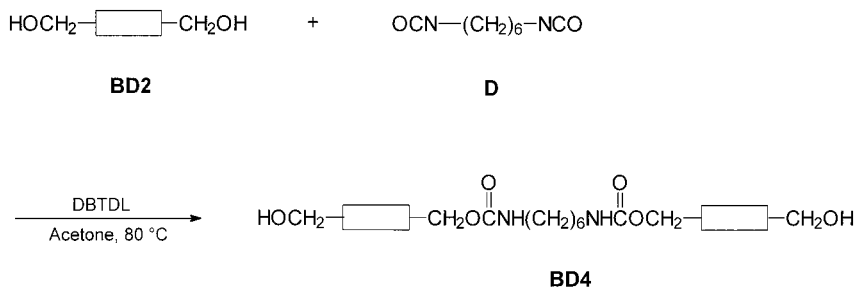
Figure 3 Chain extension of BD: a hexamethylenediisocyanate-mediated urethane coupling of 2 BD2-units.

der to connect 2 BD2-units (BD4), 3 BD2-units (BD6), and 4 BD2-units (BD8), respectively. The urethane coupling was catalyzed by 0.01 wt.-% of dibutyltindilaurate (DBTDL) at 80°C. ^{1}H nuclear magnetic resonance (^{1}H-NMR) spectroscopy of the reaction products proves the formation of urethane links. The individual peaks in the spectra of BD2, BD4, BD6, and BD8 [Fig. 4(a)] as assigned in the chemical structure [Fig. 4(b)] show a decrease of the signal of the protons in α-position to the hydroxy endgroups (b) at 3.6 ppm with increasing molecular weight and the appearance of a new peak (c) at 3.1 ppm of the newly formed urethane group generated by the protons in α-position to the nitrogen. The formation of the urethane group is also proved by the new broad peak (a) at approximately 4.8 ppm, which arises from the signal of the hydrogen bonded directly to nitrogen.

The molecular weight of all modifiers used in this investigation was determined by vapor pressure osmometry (VPO) using a Perkin–Elmer 115 vapor pressure osmometer. The glass transition temperature was measured by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-7 at a heating rate of 20 K/min. The data corresponding to the midpoint of the glass transition step are shown in Table I. Whereas glass transition temperatures of BD1 and BD2 are −30 and −19°C, respectively, BD4 and BD6 show glass transition temperatures of −7 and −1°C, respectively, which is not far from ambient temperature. BD8 exhibits an even higher glass transition temperature of +6°C. In comparison, standard CTBN rubber shows a significantly lower glass transition temperature of about −50°C.

DGEBA was mixed with different amounts of BD solution in acetone to produce the final rubber concentrations shown in Table II. After complete removal of the acetone 92 mol% HHPA with respe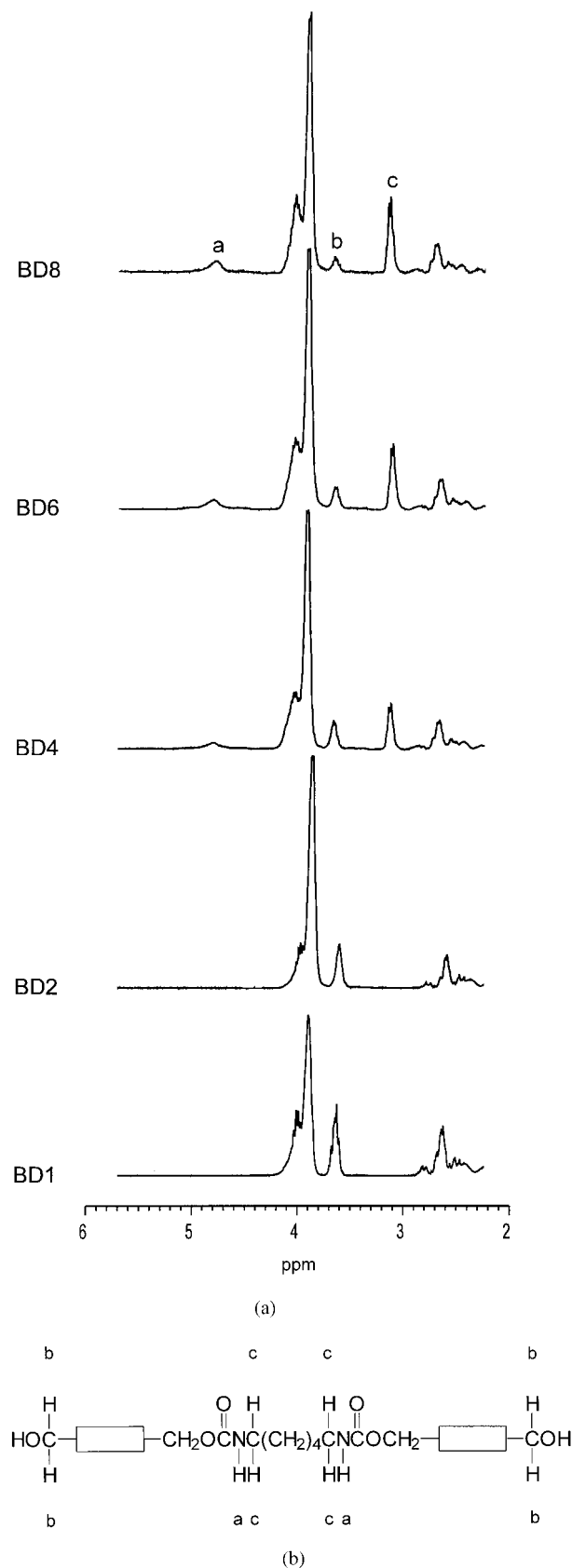ct to DGEBA was added, and the mixture was degassed in vacuum at 80°C. Before pouring the mixture into a steel mold preheated to 90°C, 1.8 mol% DBA with respect to DGEBA was added and solved by gentle stirring for 5 min.

Curing was performed at 150°C for 3 h, followed by 1 h at 180°C. Before removing the mold from the oven, it was allowed to cool down to room temperature. The modified resins containing various amounts of BD of different molecular weight are listed in Table II. Optical appearance of the resulting materials, also given in Table II, is related to the molecular weight of the rubber used for modification. Opaque materials are considered as multiphase resins with phase separation of the modifier taken place during the curing process, whereas translucent materials are considered to be single phase resins, as discussed in more detail in context with the experimental results.

TESTING METHODS

The epoxy resins were examined by a variety of different mechanical testing methods. Short-term tensile properties, such as tensile strength and Young's modulus, were measured in an Instron 4204 servohydraulic testing machine using dog-bone-shaped tensile bars with 4-mm thickness, 10-mm width, and 60-mm gauge length cut from the epoxy sheets. The tensile experiments were performed at a crosshead speed of 5 mm/min. A strain gauge extensometer was applied for strain measurement. Young's modulus E was taken from the slope of the initial linear region of the measured stress-strain curve at 0.1% strain. The maximum stress of the stress–strain curve was taken as the tensile strength σ_B.

The fracture toughness K_{lc} was determined by tensile experiments on compact tension (CT) specimens in a Zwick tensile testing machine at a

(a)

(b)

Figure 4 (a) Characterization of chain-extended BD by ^{1}H nuclear magnetic resonance spectroscopy. (b) Assignment of peaks in (a) to the structure of the chain-extended BD.

crosshead speed of 1.8 mm/min. The dimensions of the CT specimens were thickness B equals 4 mm, height $2H$ equals 8 mm, and effective width W equals 8 mm. The precrack was sharpened by pushing a razor blade into the saw notch. The effective crack length a was determined by measuring in a travelling microscope after the tensile test. The maximum load P_c measured in the experiment was taken to calculate K_{lc} according to eq. (1).

$$K_{lc} = \frac{P_c \cdot (2W + a)}{(B \cdot (W - a))^{3/2}} \cdot Y\left(\frac{a}{W'}, \frac{H}{W}\right) \qquad (1)$$

The geometrical factor $Y\left(\dfrac{a}{W'}, \dfrac{H}{W}\right)$ valid for compact tension specimens was calculated according to Srawley and Gross.[14]

Dynamic mechanical analysis (DMA) was performed using a Rheometrics RSA II Solids Analyzer equipped with a dual cantilever specimen mounting tool. A frequency of 1 Hz and a strain level of 0.1% were applied to record the storage modulus E', as well as the loss tangent $tg\ \delta$, scanning a temperature range from -120 to 160°C at a heating rate of 3 K/min. The dimensions of the specimens were $50 \times 4 \times 3$ mm^3. The maximum energy loss, that is, the α-peak maximum of the $tg\ \delta$-versus-T-graph was taken as an approximation of the glass transition temperature T_g of the tested materials since this method is widely used in the literature.[15,16]

Some fracture surfaces of the tensile test specimens were examined by scanning electron microscopy (SEM) using a CamScan electron microscope operating at an accelerating voltage of 25 kV. In order to prevent charging of the samples and to protect the surface structures, the surfaces were coated with copper metal using a low energetic sputtering process.[17]

RESULTS AND DISCUSSION

For different BD-modified systems fracture toughness K_{lc} is shown in Figure 5 as a function of the rubber content. The graphs can be associ-

Table I   Characterization of α,ω-Oligo(butylmethacrylate)diols Used in This Study

Denotation of Rubber	Molecular Weight (g/mol)	Glass Transition Temperature T_g (°C)
BD1	1250	−30
BD2	2100	−19
BD4	3700	−7
BD6	5100	−1
BD8	6500	+6

ated with 2 groups, one corresponding to multiphase resins (modified with BD4, BD6, and BD8), and the other to single-phase resins (modified with BD1 and BD2). While the addition of 10 wt% BD1 or BD2, respectively, leads to almost negligible increase in fracture toughness compared to the unmodified resin, adding BD rubber with molecular weights higher than 3000 g/mol causes the fracture toughness to increase significantly. The increase in fracture toughness intensifies with increasing molecular weight of the rubber, as can be taken from the shift of the graphs in Figure 5.

For many structural applications modulus and strength decide the suitability of a material. Thus, toughness improvement of a suitable material must be performed without significant loss in modulus and strength.

Figures 6 and 7 show the Young's modulus E and the fracture strength σ_B, respectively, as functions of rubber content. As a general trend, both E and σ_B decrease with increasing rubber content as known for most of the modified resins. Examining Figure 6 in more detail reveals at rubber contents of more than 10 wt% that the softening effect increases with the increasing molecular weight of the rubber. The measured moduli vary between 2900 and 2300 MPa for all tested materials. In the case of optimum modification (10BD6), E does not drop below 2600 MPa.

A closer look at Figure 7 reveals that the decrease of fracture strength of single-phase resins

Table II   Materials Synthesized in This Study

Denotation	Modifier	Content of Modifier (Wt%)	Optical Appearance[a]
5BD1	BD1	5	t
10BD1		10	t
15BD1		15	t
20BD1		20	t
5BD2	BD2	5	t
10BD2		10	t
15BD2		15	t
20BD2		20	t
5BD4	BD4	5	o
7.5BD4		7.5	o
10BD4		10	o
15BD4		15	o
5BD6	BD6	5	o
7.5BD6		7.5	o
10BD6		10	o
15BD6		15	o
5BD8	BD8	5	o
10BD8		10	o

[a] t indicates a translucent appearance.
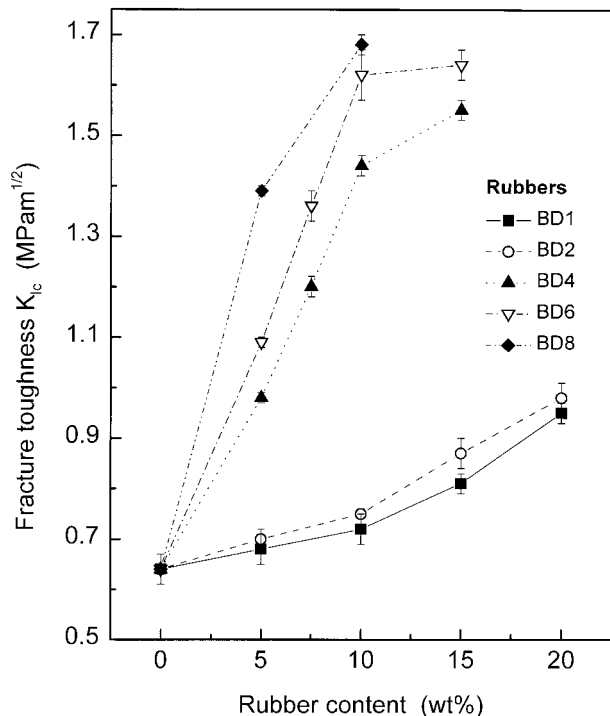o indicates an opaque appearance.

Figure 5   Fracture toughness K_{Ic} versus the rubber content of epoxy resins modified with methacrylate-based rubbers of different molecular weights.

at low rubber concentrations up to 10 wt% is less than that of multiphase resins; whereas at higher concentrations, this behavior changes. At 10 wt% modifier concentration of the rubbers BD1 and BD2, the resins have almost the same strength of about 80 MPa, slightly below the fracture strength of the neat resin (87 MPa), while that of resins modified with rubbers, leading to phase separation strength, is somewhat lower, between 70 (BD8) and 76 MPa (BD4). A further increase of rubber content in single-phase materials leads to a dramatical drop in strength. At a rubber content of 20 wt% strength, values of 41 (BD1) and 45 MPa (BD2) are exhibited. In comparison with this, multiphase materials show a less steep drop in strength with increasing rubber content.

Regardless of the reduction in stiffness and strength, the effects due to the addition of noticable amounts (up to 10 wt%) of suitable rubbers, such as BD6, is still tolerable. For example, 10BD6 shows a stiffness of about 2600 MPa and a fracture strength of 73.3 Pa. Compared to the neat resin, these values correspond to a loss in stiffness of 11% and in strength of 16%, respectively, while fracture toughness increases by 150%.

Another important precondition for the use of materials in structural application is the knowledge of the temperature behavior of mechanical properties, which can be determined by DMA measurements.

Figure 8 shows E' as well as tg δ of the neat resin, 10BD2, 10BD4, and 10BD6 for a temperature range from -120 to $+160°C$. The graph of tg δ for the unmodified resin shows 2 significant peaks, which are typical for epoxy resins.[18] A comparatively low and broad peak is located at about $-70°C$ and is related to the β-relaxation of the matrix. The beginning of overall mobility of the network is related to the α-relaxation process, which results in an intense narrow tg δ peak. This relaxation is accompanied by a dramatic drop of E', resulting in a stiffness loss by a factor of more than 2 decades. 10BD2 shows a very similar behavior. The only difference compared to the unmodified resin is the beginning of decrease in storage modulus at a lower temperature and, accordingly, a shift of the α-relaxation peak to a lower temperature. On the other hand, 10BD4 shows an additional broad peak at about $+10°C$. This peak is related to relaxation processes in the separated rubber phase. A sim-
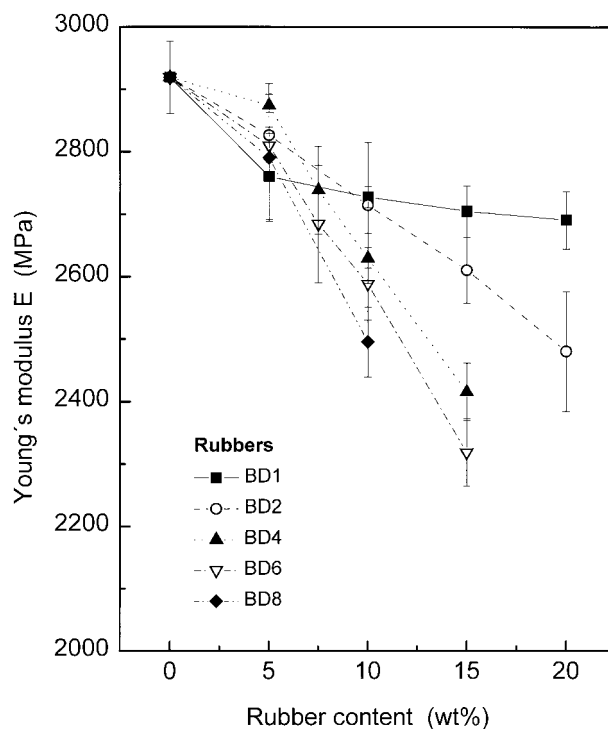

Figure 6   Young's modulus E versus the rubber content of epoxy resins modified with methacrylate-based rubbers of different molecular weights.
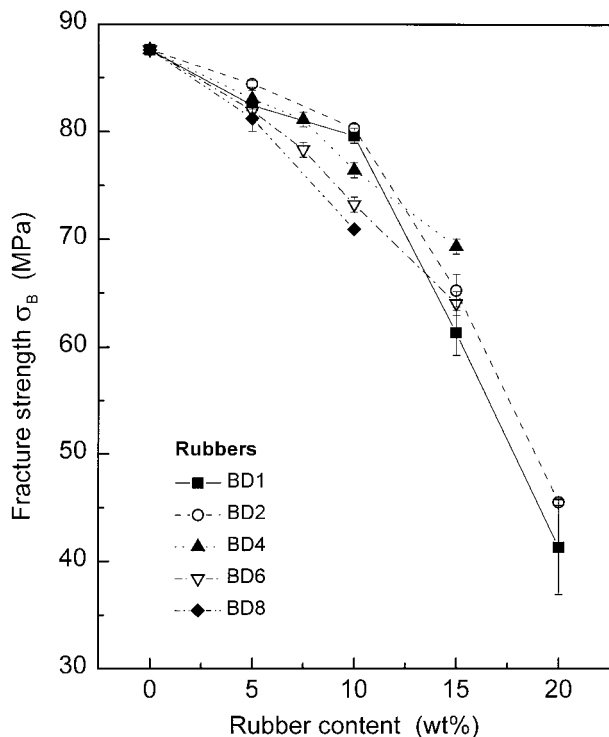
Figure 7 Fracture strength σ_B versus the rubber content of epoxy resins modified with methacrylate-based rubbers of different molecular weights.

ilar but more intensive peak due to rubber relaxation is shown by 10BD6. The peak is much broader than that of 10BD4, and the maximum is shifted to about $-10°C$.

Comparison of the E' curves of the neat resin, 10BD2, 10BD4, and 10BD6 reveals another interesting detail concerning the scale of storage modulus loss at increasing temperature. Whereas at room temperature E' of all of these 4 resins is in a small range between 2200 and 2400 MPa, the temperature at which E' has decreased to 1000 MPa is 125°C in the case of the neat resin, 115°C in the case of 10BD6, and 104°C in the case of 10BD2 and 10BD4. Actually, modification of 10 wt% BD6 leads to a loss in storage modulus at a considerably lower temperature compared to neat resin, but compared to lower-molecular-weight modifiers like BD2 or BD4, it is clearly smaller. T_g is usually considered as an estimation of the softening point of the matrix. In Figure 9, T_g of the resin is shown as a function of rubber content. As a general trend, T_g decreases approximately linearly with increasing rubber content, but the slopes of the resulting straight lines become less negative with the increasing molecular weight of

the rubber. This indicates that the amount of rubber that is integrated into the matrix decreases with the increasing molecular weight of the rubber, though, even at high molecular weight, T_g is reduced by a few Kelvin compared to the unmodified resin, indicating that phase separation even at a high molecular weight of rubber is not complete. The Fox equation (eq. 2),[19] as follows, can be used to roughly estimate the amount of rubber that does not take part in phase separation process, becoming an integrated part of the matrix instead:

$$\frac{1}{T_{mod}^{res}} = \frac{1 - W}{T_{matrix}} + \frac{W}{T_{mod}} \qquad (2)$$

In eq. (2), T_{mod}^{res} is the glass transition temperature of the modified resin, T_{mod} is the glass transition temperature of the rubber (taken from Table I), T_{matrix} is the glass transition of the neat resin, and W is the weight fraction of the modifier being incorporated in the matrix. Figure 10 shows W as a function of the overall modifier content for different rubbers. The straight line (b in Fig. 10) indicates the theoretical case of all rubber being integrated in the matrix. The graph of resins modified with BD1 runs in close proximity to this line, indicating that almost all added BD1 is solved in the matrix and a single phase morphology is present. However, the graphs of multiphase materials toughened with BD4, BD6, or BD8 show distinct deviations from line b (in Fig. 10), indicating that only a small amount of rubber is solved in the matrix, whereas most of the rubber is separated from the matrix phase. For materials toughened with BD6 or BD8, this effect is stronger than that of BD4-modified resins. In all cases, small amount of rubber remains solved in the matrix so the phase separation process is incomplete in any case. The graph of BD2-modified resins is located between the graph of BD1, representing a single-phase morphology, and the graph of BD4, representing a multi-phase morphology, supporting the assumption that the morphology of BD2-modified materials is located in the area of transition between single- and multiphase morphology. Moreover, the existence of a minimum amount of rubber not taking part in phase separation, even if a further increase of molecular weight takes place, is supported by the fact that the graphs of BD6 and BD8 are located in close proximity.

Nevertheless, effective toughening can be achieved without a dramatic drop of T_g. 10BD6,
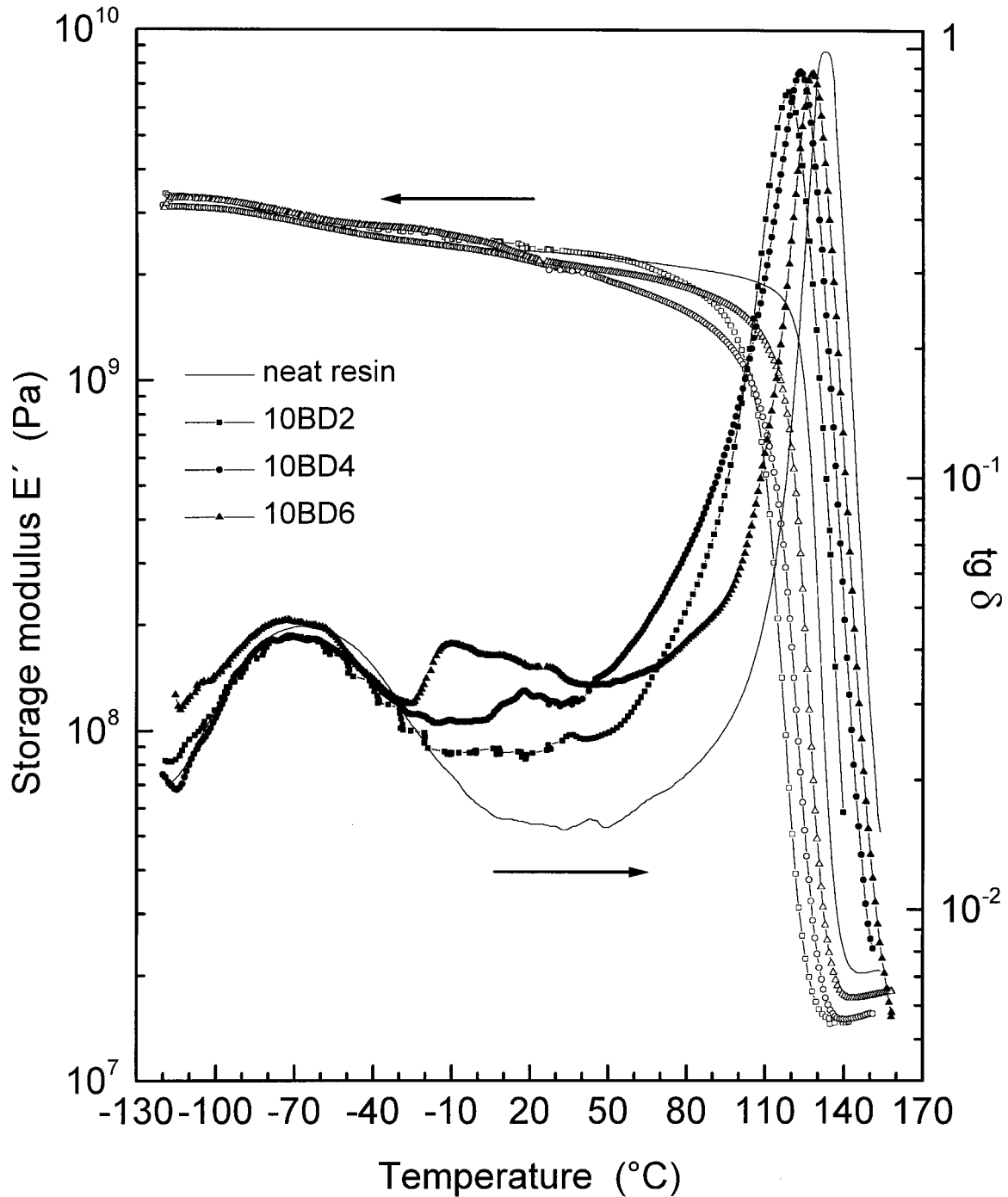
Figure 8 Storage modulus E' and loss tangent $tg\ \delta$ of the neat resin, 10BD2, 10BD4, and 10BD6 as a function of temperature.

for example, exhibits a glass temperature of 128°C, which is only 5 K less than that of the neat resin.

Phase separation of the rubber during the curing process is a decisive condition for effective toughening.[20] While the resins modified with BD4, BD6, and BD8, having significantly higher K_{lc} values than the neat resin generally exhibit phase separation, those modified with BD1 and BD2 do not show any phase separation, even at high rubber concentrations up to 20 wt%. This is illustrated by micrographs of the fracture sur-
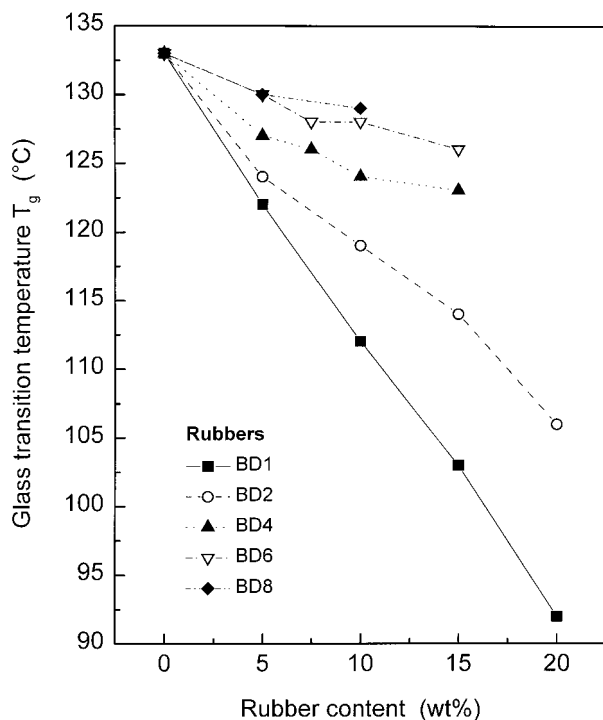
Figure 9 Glass transition temperature T_g versus the rubber content of epoxy resins modified with methacrylate-based rubbers of different molecular weights.

faces of selected tensile specimens [Fig. 11(a)–(e)]. While BD1 and BD2 show a single phase [Fig. 11(a) and (b)], BD4, BD6, and BD8 exhibit separated rubber particles [Fig. 11(c)–(e)]. The increase of fracture toughness using BD1 or BD2 is very small since the rubber has become a molecularly integrated part of the network upon curing. Thus, various energy-absorbing mechanisms acting in phase-separated materials, especially matrix shear yielding and rubber cavitation processes, cannot operate in the absence of phase-separated rubber particles. The slight increase of fracture toughness merely arises from the effect of matrix flexibilization due to a decrease in crosslink density.[20,21]

The increase of fracture toughness of the multiphase systems is related to the size of the separated rubber particles. The rubber particle size increases with an increasing rubber amount as well as with an increasing molecular weight of the rubber in all of these systems but 15BD6 and 10BD8. Simultanously, the fracture toughness increases; however, it is not possible to exactly correlate fracture toughness and rubber particle size.

Rubber particle size is determined mainly by 2 competing effects, which strongly depend on cur-

ing temperature. On the onehand, phase separation is thermodynamically driven by the initial compatibility between the resin-hardener mixture and the rubber, which can be quantified by applying the concept of solubility parameters[20] and the change of solubility parameter difference with increasing molecular weight of the resin upon curing. On the other hand, the buildup of molecular weight or the gelation process, respectively, determined by the reactivity of the system impedes diffusion and, thus, phase separation.[22,23]

The series of micrographs in Figure 11 show an interesting change in morphology with an increasing molecular weight of the toughener additionally to the change in phase separation between 10BD2 [Fig. 11(b)] and 10BD4 [Fig. 11(c)]. Comparing the fracture surfaces of 10BD6 [Fig. 11(d)] and 10BD8 [Fig. 11(e)], another noticable difference in morphology becomes evident. In 10BD6, discrete modifier microspheres of homogenous appearance are seen, while in 10BD8, the modifier particles and matrix holes of irregular
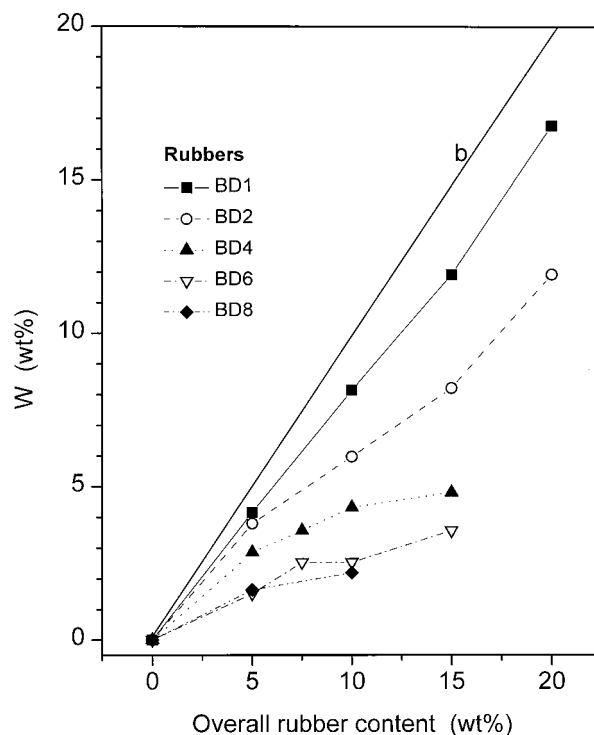

Figure 10 Weight fraction W of rubber being incorporated in the matrix versus the overall rubber content of epoxy resins modified with methacrylate-based rubbers of different molecular weights. The straight line (b) indicates the theoretical case that W equals the overall rubber content.
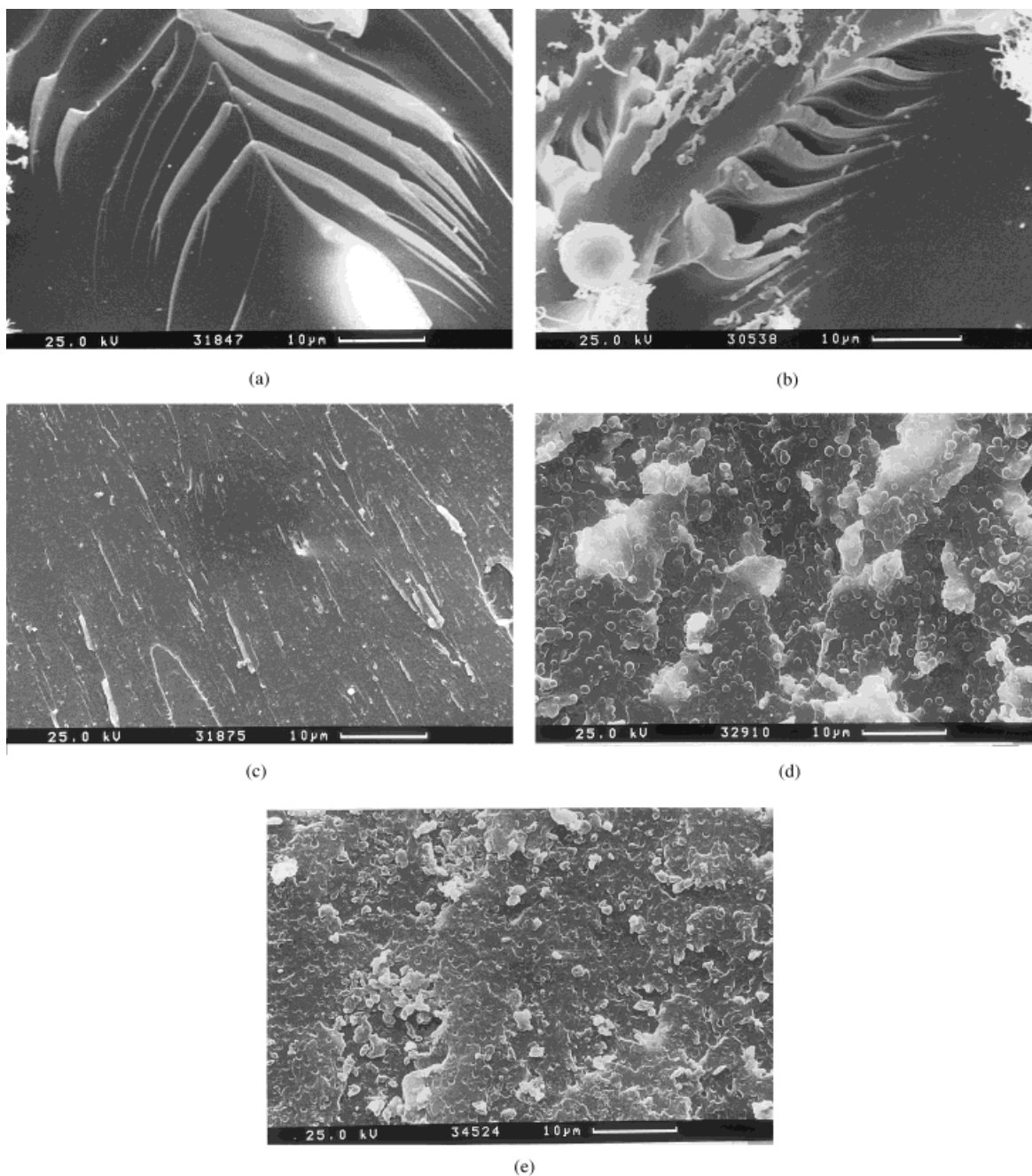
Figure 11   Micrographs of fracture surfaces: (a) 10BD6; (b) 10BD2; (c) 10BD4; (d) 10BD6; (e) 10BD8.

shapes significantly differ from microspheres. Though the origin of these differences is not fully understood, the irregular structure of 10BD8 indicates that the morphology of the system is related to the area of transition from resin matrix–separated modifier to cocontinuous structure of resin and modifier. A similar morphology difference is observed comparing 10BD6 and 15BD6.

Both materials exhibit almost the same fracture toughness of about 1.6MPa m$^{-1/2}$.

An optimal rubber molecular weight as well as an optimal rubber content for toughening seems to exist. The molecular weight of the rubber, resulting in the maximum fracture toughness, is in the range of 5000 to 6000 g/mol. The rubber content of the material should not exceed 10 wt% for

optimal toughening. A further increase of either molecular weight of the rubber or rubber content might lead to further toughness enhancement, but this effect is comparably small and cannot be justified due to severe deterioration of other mechanical properties.

CONCLUSION

In this work, the effectiveness of α,ω-oligo(n-butylmethacrylate)diols (BD) to toughen epoxies has been investigated. Liquid rubber toughening agent of a different molecular weight was synthesized and blended with a liquid bisphenol-A-based epoxy resin in various amounts. Curing was performed using hexahydrophthalic anhydride. Toughness, stiffness, and strength of the resulting materials were determined accompanied by dynamic mechanical, as well as fractographic, analysis. From the results of these experiments, the following conclusions have been drawn.

1. Phase separation upon curing strongly depends on the molecular weight of the rubber. Epoxies modified with BD rubber of low molecular weight (lower than 3500 g/mol) are single-phase materials, whereas rubber of molecular weight higher than about 4000 g/mol leads to the formation of multi-phase materials with micron-sized spherical rubber particles embedded in the epoxy matrix. The transition between the single-phase morphology and the multi-phase morphology with an increasing molecular weight of the rubber is rather continuous.
2. Multi-phase morphology is an important precondition for effective toughness enhancement. Applying low-molecular-weight rubber without phase separation results only in marginally increased toughness.
3. Blending with BD enables toughening, with only small reductions of other mechanical properties, such as Young's modulus, tensile strength, and glass transition temperature. Slight flexibilizing is due to the fact that phase separation is not complete, even if very high molecular weights of the rubber are used.
4. Increasing molecular weight as well as increasing content of the rubber lead to increasing the toughness of the modified epoxy provided that a multi-phase morphology

is formed. However, exceeding a particular BD rubber content as well as exceeding a maximum molecular weight of the rubber, the morphology of the resulting materials changes from rubbery particles within a stiff matrix towards a cocontinuous structure. This morphology change leads to reductions in mechanical properties.

The best toughening of the epoxy resin has been achieved using BD of a molecular weight of about 5100 g/mol in a concentration of 10 wt% increasing fracture toughness K_{lc} by 150% compared to the neat resin. On the other hand, reductions of stiffness (-11%) and strength (-16%) are comparably small. Glass transition temperature reduction (-5 K) is almost negligible.

These results show that α,ω-oligo(n-butylmethacrylate)diols are suitable materials to toughen epoxy resins. In comparison to traditional CTBN rubber, acrylic rubbers do not contain olefinic bonds in the rubber backbone, which are sensitive towards oxidation. In order to compete with CTBN, the glass transition temperature of the BD rubbers should be lowered by tailoring special methacrylate copolymers.

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