Ultimate toughness of amorphous polymers

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ULTIMATE TOUGHNESS OF AMORPHOUS POLYMERS

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Abstract: The deformation and toughness of amorphous glassy polymers is discussed in terms of both the molecular network structure and the microscopic structure at length scales of 50-300 nm. Two model systems were used: polystyrene-poly(2,6-dimethyl-1,4-phenylene ether) blends (PS-PPE; where PS possesses a low entanglement density and PPE a relatively high entanglement density) and epoxides based on diglycidyl ether of bisphenol A (DGEBA) with crosslink densities comparable with up to values much higher than the thermoplastic model system. The microscopic structure was controlled by the addition of different amounts of non-adhering core-shell-rubber particles. Toughness is mainly determined by the maximum macroscopic draw ratio since the yield stress of most polymers approximately is identical (50-80 MPa). It is shown that the theoretical maximum draw ratio, derived from the maximum (entanglement or crosslink) network deformation, is obtained macroscopically when the characteristic length scale of the microstructure of the material is below a certain dimension; i.e. the critical matrix ligament thickness between added non-adhering rubbery particles ('holes'). The value of the critical matrix ligament thickness (ID_c) uniquely depends on the molecular structure: at an increasing network density, ID_c increases independent of the nature of the network structure (entanglements or crosslinks). A simple model is presented based on an energy criterion to account for the phenomenon of a critical ligament thickness and to describe its strain-rate and temperature dependency.

INTRODUCTION

The last two decades have seen impressive progress concerning the development of polymer materials possessing ultimate properties in terms of modulus and strength (ref.1-3). These maximum properties were achieved upon aligning and extending the polymer chains. For flexible macromolecules (notably Ultra-High-Molecular-Weight Polyethylene, UHMW-PE), this was realized by stretching the polymer network to its maximum (ref.2). The maximum extension ratio is determined by the molecular weight between network loci of enhanced friction (molecular weight between entanglements, M_e -or, analogously, for thermosets molecular weight between crosslinks, M_c -). According to classical rubber elasticity theory (ref.4), the maximum draw ratio of a network is proportional to:

$$\lambda_{\max} \sim M_e^{1/2} \quad (1)$$

Recently, we focused our attention on the achievement of the ultimate toughness of polymeric materials based on the above understanding of the drawing behaviour of entangled or crosslinked networks. It is postulated that, since the yield stress of a great variety of amorphous glassy polymers approximately is identical (50-80 MPa), toughness is determined mainly by the maximum elongation at break. The characteristics of the network topology are mainly determined by the intra-molecular structure of the polymer molecule (chain stiffness). Based on these simple arguments, polystyrene (PS) should be one of the more ductile amorphous polymers, since it possesses a molecular weight between entanglements, M_e , of $19.1 \text{ kg mole}^{-1}$, resulting in a theoretical maximum draw ratio of 4.2 (320% strain-at-break).

Kramer et al. have determined the maximum draw ratio of various amorphous polymers on the microscopic level (ref.5,6). They analyzed a large number of glassy polymers by measuring the local extension ratio of the material inside a craze-fibril or shearing zone, and found a close agreement between the theoretical value (according to equation (1)) and the microscopically measured strain.

Commonly PS, however, is a very brittle polymer that exhibits a macroscopic strain-at-break typically of less than 5%. The macroscopic strain-to-break is governed by a non-homogeneous deformation behaviour (stress and strain localizations). Thus, in order to extend the high strain levels from a microscopic to the macroscopic level, the polymer microstructure has to be controlled so as to prevent catastrophic fracture anywhere in the sample. Hence, it is necessary that locally initiated deformation continues throughout the complete sample without premature fracture of deformed areas. Previously, we have shown that the macroscopic strain-to-break of PS can be increased from less than 5% up to 200% by introducing approximately 60 vol% of holes in the polymeric material (ref.7). The critical dimension of the polymeric material between the holes, below which the polymer behaves in a very ductile manner, is called the critical ligament thickness and depends on the type of polymer. In addition, the value of the critical ligament thickness proves to be a well defined function of the entanglement or network density (ref.8,9).

In this paper we present an overall picture of deformation and toughness of polymeric systems. Both, neat and rubber-modified thermoplastic and thermosetting polymers will be discussed with a focus on the macroscopic toughness (read: strain-at-break) in dependence of the molecular network structure and the microstructure (ligament thickness). The molecular weight between entanglements (M_e) is varied by the compositions of the homogeneously miscible system polystyrene-poly(2,6-dimethyl-1,4-phenylene ether) (PS-PPE) (ref.10). For the thermosetting polymers the molecular weight between crosslinks can be varied by changing the monomer molecular weight of the epoxide resin used (ref.9).

Rather loose chemical networks were chosen in this investigation in order to obtain values of M_e and M_c of the same order of magnitude, in terms of the network density, thus elucidating the principle similarity in the deformation behaviour of both types of networks. A non-adhering core-shell-rubber of constant particle size is used in order to control the interparticle distance in the case of rubber-modified polymers. Toughness was determined via slow-speed tensile testing as well as via high-speed notched tensile tests at room temperature. As stated, this paper intends to provide an overall insight into the principles of deformation and toughness of polymers. Hence, a detailed description of the experimental part is omitted in order to focus the reader's attention fully on the general aspects of deformation and toughness of amorphous glassy polymers. For a detailed description of the experimental procedures is referred to a series of previously published papers on this subject (ref.7-9).

THERMOPLASTICS (physical networks)

The entanglement molecular weight (M_e) can be adjusted between the value of pure PS ($19.1 \text{ kg mole}^{-1}$) and of pure PPE (3.4 kg mole^{-1}) by changing the relative volume fractions of both components in this miscible blend. The characteristics of the polymer network are determined in the melt where the secondary bonds are excessively weak. By determining the rubber plateau modulus (G_{No}), with dynamic mechanical thermal analysis, the molecular weight between entanglements can be calculated using equation (2):

$$M_e = \frac{\rho RT}{G_{No}} \quad (2)$$

where ρ is the density of the amorphous glass, R is the gas constant and T is the reference temperature (ref.11). The entanglement density (v_e) can be calculated with:

$$v_e = \frac{\rho N_A}{M_e} \quad (3)$$

where N_A is Avogadro's number. This yields a value of v_e of 3×10^{25} chains m^{-3} for pure PS and a value of 13×10^{25} chains m^{-3} for pure PPE.

With equation (1), the theoretical maximum draw ratio, λ_{max} , can be calculated from the experimentally determined molecular weight between entanglements. In Fig. 1 the experimentally determined macroscopic strain-to-break data of various PS-PPE blends are shown as a function of the core-shell-rubber concentration present in the matrix, as obtained from slow-speed tensile testing (5 mm min^{-1}) (ref.8). The core-shell-rubber (particle size: $0.1\text{-}0.3 \text{ }\mu\text{m}$) is present to generate locally thin ligaments since the polymethylmetacrylate shell does not attach to the PS, respectively the PS-PPE, matrix (ref.12). The macroscopic strain-to-break of pure PS is less than 5% (not incorporated in Fig. 1). Only if 60 wt% of the non-adhering core-shell-rubber is added to PS (curve A) the macroscopic strain-at-break is significantly increased ($\approx 200\%$). Scanning electron microscopy revealed that the rubbery particles still form the dispersed phase even in these

highly filled systems (ref.7).

The average matrix ligament thickness where the brittle-to-ductile transition occurs for PS was calculated from the rubber volume fraction and particle size assuming a body-centred-cubic lattice. PS modified with 50 wt% core-shell-rubber contains ligaments of an average thickness of $0.06\ \mu\text{m}$ and possesses a typically brittle fracture behaviour. PS modified with 60 wt% rubber (average ligament thickness: $0.04\ \mu\text{m}$) demonstrates a ductile deformation behaviour. Hence, the critical matrix ligament thickness is about $0.05\ \mu\text{m}$ for PS. If adhering core-shell-rubbers are used (e.g. with a polystyrene shell (ref.7)), even blends containing 60 wt% rubber show a brittle fracture behaviour, thus emphasizing that 'holes' are locally needed. Obviously, particles that are firmly attached to the matrix do not form a thin matrix ligament that can deform without any interference of the rubbery phase.

Fig. 1: Strain-at-break of core-shell-rubber-modified PS-PPE blends vs rubber concentration with parameter the matrix composition (PS-PPE): A: 100-0; B: 80-20; C: 60-40; D: 40-60; and E: 20-80

Fig. 2: Strain-at-break of core-shell rubber-modified epoxides vs rubber concentration with parameter the molecular weight between crosslinks: A: $6.8\ \text{kg mole}^{-1}$; B: $4.4\ \text{kg mole}^{-1}$; C: $1.6\ \text{kg mole}^{-1}$; and D: $0.9\ \text{kg mole}^{-1}$

Increasing the network density of the matrix (i.e. addition of PPE) results in: (i) a decrease of the level of ductility in the tough region and (ii) a shift of the critical rubber concentration to lower values hence, a shift of the critical (local) thickness to higher values. Interestingly, the macroscopic strain-to-break in the ductile region does not increase any further if the matrix ligament thickness is already below its critical value. For the PS-PPE 20-80 w-w blend (curve E) the maximum macroscopic strain-at-break is already obtained in the neat blend (no rubber present). Adding core-shell rubbery particles to this PS-PPE blend does not result in an increase in strain-to-break, therefore, this blend does not show a brittle-to-ductile transition. However, under more extreme testing conditions (high-speed, or notched tensile testing (ref.13)) a brittle-to-ductile transition becomes noticeable, as expected.

THERMOSETS (chemical networks)

Crosslinked epoxides based on diglycidyl ether of bisphenol A (DGEBA) that are stoichiometrically cured with 4,4'-diamino diphenyl sulphone (DDS) possess a molecular weight between crosslinks (M_c) typically in the range of 0.3-7 kg mole⁻¹ (determined analogous to the value of M_c using equation (2)). In terms of network density these M_c values correspond to 8×10^{25} - 235×10^{25} chains m⁻³, i.e. network densities ranging from values comparable with, up to values much higher than the thermoplastic PS-PPE model system.

In Fig. 2 the macroscopic strain-at-break data of various neat and core-shell-rubber modified crosslinked epoxides, measured in slow-speed tensile testing are shown (for experimental details see ref. 9). Curves A and B correspond to epoxides having a rather high value of M_c (curve A: $M_c = 6.8$ kg mole⁻¹; curve B: $M_c = 4.4$ kg mole⁻¹). The macroscopic strain-at-break of these epoxides is constant, independent of the amount of core-shell-rubber added to the system. The strain-to-break data of the pure epoxides are omitted in Fig. 2 because the reliability of these data is rather poor due to the high defect sensitivity of the samples. Decreasing the molecular weight between crosslinks (Fig. 2 curve C, respectively curve D) results in a decrease of the macroscopic draw ratio (read: strain-to-break) analogous to the results obtained with the thermoplastic blends of PS and PPE where a decrease in M_c also resulted in a lower value of the maximum macroscopic strain-at-break (see Fig. 1).

MACROSCOPIC DRAW RATIO

In Fig. 3 the strain-to-break data of Fig. 1 and 2 are combined: the maximum macroscopic draw ratio, λ_{macr} , is plotted vs the network density. The network density is expressed in terms of respectively entanglement density (thermoplastic PS-PPE system) or crosslink density (thermosetting epoxide system). As can be inferred from Fig. 3, the maximum macroscopic draw ratio decreases with a decreasing molecular weight between entanglements (for the system PS-PPE, open circles) or crosslinks (for the thermosetting system, filled circles). The drawn curve in this figure is calculated according to the maximum draw ratio of a single network strand (equation (1)). The experimental data all are systematically situated below the drawn curve.

Also experiments of Kramer et al. showed the same discrepancy (ref.5,6) as observed in Fig. 3. These authors measured the draw ratio inside a shear deformation zone and inside a craze fibril (i.e. microscopic level). Comparing these microscopic strain-to-break data with the theoretical maximum draw ratio of the various polymers shows, in the case of the crazing mechanism, a clear one-to-one agreement. For shear deforming polymers only 60% of the theoretical draw ratio is measured inside a shear deformation zone. The reason for this discrepancy is explained by the rather naive assumption of taking one single network

strand in order to describe a fully three dimensional network (ref.6). The close agreement in the case of the crazing mechanism is only misleading because in this situation the network structure is partly destroyed during the formation of the craze structure. In Fig. 3 also the curve according to $0.6 \cdot \lambda_{\max}$ is drawn (dashed curve). A good correlation is obtained between the experimental data and the drawn dashed curve. Obviously, the distribution in network density limits the maximum macroscopic draw ratio to 60% of the theoretical draw ratio of the average network density. Any network arguments only lead to higher predicted values of the network extension ratio.

Fig. 3 : Draw ratio vs network density (entanglement and/or crosslink density). For details see text

Fig. 4 : Notched tensile toughness of core-shell-rubber modified epoxides vs rubber concentration with parameter the molecular weight between crosslinks: A: 6.8 kg mole⁻¹; B: 4.4 kg mole⁻¹; C: 1.6 kg mole⁻¹; and D: 0.9 kg mole⁻¹ (ref. temperature: 20°C)

From Fig. 3 it is clear that the maximum macroscopic draw ratio is governed by the molecular network structure. The entanglement (or, alternatively, crosslink) network governs the deformation behaviour independent of the nature of the network: physical network loci or chemical crosslinks. Data obtained from the thermoplastic PS-PPE system perfectly match with the data obtained from the epoxide system. Interestingly, there is even some overlap in both systems, which further corroborates the previous statement.

CRITICAL LIGAMENT THICKNESS

As already mentioned during the discussion of Fig. 1, the maximum macroscopic strain-to-break in thermoplastic systems often can be obtained only if the material is filled with a certain concentration of 'holes' (non-adhering rubbery particles). The ligaments between those holes need to have a thickness below the critical value in order to obtain the maximum value of macroscopic toughness. For the PS-PPE 20-80 w-w blend, however, no

brittle-to-ductile transition was observed, analogous to the thermosetting epoxy system. Fig. 4 shows that in the latter situation also brittle-to-ductile transitions are observed if the testing conditions are more extreme: e.g. notched samples strained at a crosshead speed of 1 m s^{-1} at room temperature (ref.9). In Fig. 4 the tensile toughness (integrated area under the recorded stress strain curve) is plotted vs rubber concentration for epoxides with distinct values of M_c . Curve A, corresponding to the epoxide with a molecular weight between crosslinks of 6.8 kg mole^{-1} shows the highest value of the notched tensile toughness in the ductile region and a critical rubber concentration of $\sim 12 \text{ vol\%}$. When the M_c value of the epoxide is lowered (curve B; $M_c = 4.4 \text{ kg mole}^{-1}$), the brittle-to-ductile transition is found at a lower rubber concentration. Thus, the critical ligament thickness increases with a decreasing molecular weight between crosslinks. Further decreasing the molecular weight between crosslinks results in a further increase of the critical interparticle distance (curve C, respectively curve D; Fig. 4). For the epoxides possessing a M_c of 1.6 kg mole^{-1} (curve C) and 0.9 kg mole^{-1} (curve D) the brittle-to-ductile transition is positioned below $5 \text{ wt\%}$ core-shell-rubber. Hence, the exact value of the critical interparticle distance can not be accurately estimated for these two epoxides using the small ($\approx 0.2 \mu\text{m}$) core-shell-rubbers. The maximum level of tensile toughness also depends on the value of M_c . In agreement with the conclusions arrived at in the discussion of Fig. 2, the maximum tensile toughness (read: macroscopic draw ratio) increases with an increasing molecular weight between crosslinks. This confirms the validity and usefulness of the concept of a maximum macroscopic draw ratio that is determined by the stretching of a network strand on the molecular level.

In Fig. 5 the values of the critical matrix ligament thickness, as obtained from slow-speed tensile tests (PS-PPE system, open circles; Fig. 1) and obtained from high-speed tensile tests (epoxide system, filled circles; Fig. 4), are plotted vs the network density.

Fig. 5: Critical ligament thickness vs network density (entanglement and/or crosslink density). For details see text

Fig. 6: Schematic view of a matrix ligament between two rubbery particles: (a) before plastic deformation; and (b) during plastic deformation

Fig. 5 clearly demonstrates that the critical ligament thickness increases with a decreasing M_c . Surprisingly, the value of the critical matrix ligament thickness for the epoxide with a M_c value of 6.8 kg mole^{-1} ($v_c = 8.7 \times 10^{25} \text{ chains m}^{-3}$), as measured during a notched high-speed tensile test, agrees well with the value obtained from slow-speed tensile testing of a PS-PPE 40-60 w-w blend ($v_c = 9 \times 10^{25} \text{ chains m}^{-3}$). Obviously, the network structure does determine not only the maximum macroscopic draw ratio but also uniquely dictates the value of the critical matrix ligament thickness, below which the maximum value of the macroscopic draw ratio is observed; and, moreover, the exact value of this critical thickness is rather insensitive to the testing conditions applied and the nature of the network structure (entanglements or crosslinks). By definition, the critical ligament thickness is the material specific thickness below which the polymer network can be stretched to its theoretical extension ratio, only (slightly) dependent on the testing conditions applied. The validity of this statement is demonstrated in ref. 13 where the notched high-speed tensile toughness of the PS-PPE system is described and compared with the slow-speed tensile data reported in this study.

In Fig. 5 also the critical ligament thickness of polycarbonate (ref.14, obtained from notched high-speed tensile tests) is shown. The comparison with the other data presented in Fig. 5 is of interest since polycarbonate represents one of the most densely entangled thermoplastic polymers known. More densely crosslinked epoxides can be easily obtained because the more practical systems possess crosslink densities far above $30 \times 10^{25} \text{ chains m}^{-3}$. In Fig. 5 no data for this class of epoxides are available yet since the exact value of the critical ligament thickness for low M_c thermosets can only be determined accurately with large rubbery particles. In order to allow for a direct comparison, in this study a constant, rather small sized, rubbery filler was chosen yielding unpractical small volume fractions for the determination of the exact value of the critical thickness at low values of M_c or M_c . The area of the right hand side of Fig. 5 will be investigated in the near future.

MODEL DESCRIPTION

The physical origin of the existence of a critical matrix ligament thickness for the occurrence of the brittle-to-ductile transition can be qualitatively understood in terms of continuation of locally initiated deformation without premature fracture of deformed areas. Hence, in order to derive a simple model describing the phenomenon of the material dependent brittle-to-ductile transition, the conditions have to be investigated that allow for a continuation of local deformation without catastrophic failure. In reference 8 a quantitative model is presented based on an energy criterion where, a comparison is made between the energy available (stored elastic energy) and the energy needed to create brittle fracture (fracture surface energy). In Fig.6 the model is schematically illustrated. The rubbery particles (see Fig. 6a), represented by the two circles, generate a matrix ligament containing elastic energy, U_{av} , proportional to the third power of d_1 (i.e. proportional to the shaded area):

$$U_{av} = \frac{\pi}{6} (d_1)^3 \frac{\sigma_y^2}{2 E_1} \quad (4)$$

where σ_y is the yield stress and E_1 is the Young's modulus of the matrix. The potential fracture surface is proportional to the surface of a circle of diameter d_2 (see Fig. 6b). The criterion for fracture is $d_2 = d_1 / \sqrt{(\lambda_{\max})}$ since, this represents the smallest potential fracture surface and, therefore, the most critical situation with respect to brittle fracture. Hence, the energy, U_{re} , required to create a brittle fracture can be estimated to be:

$$U_{re} = 2 \frac{\pi}{4} (d_2)^2 \Gamma \quad (5)$$

where Γ is the surface energy of the polymeric matrix material. Equating the available elastic energy with the required surface energy results in an expression of the critical ligament thickness, d_{lc} , in dependence of several material parameters, i.e. network density (entanglement and/or crosslink density), theoretical draw ratio, Young's modulus and yield stress (see ref. 8 for a more detailed description of the model):

$$d_{lc} = ID_c = \frac{6 (\gamma + k_1 v_e^{1/2}) E_1}{\lambda_{\max} \sigma_y^2} \quad (6)$$

where k_1 is a constant ($k_1 = 7.13 \times 10^{-15} \text{ J chain}^{-1/2} \text{ m}^{-1/2}$ ref. ⁸) and γ is the Van der Waals surface energy.

The curve in Fig. 5 is drawn according to the simple model (equation (6)). Especially in the region of low network densities, the model predictions agree well with the experimental values of the critical ligament thickness. For higher network densities a slight deviation is observed between the predicted and experimental values of the critical ligament thickness. The latter is probably due to an overestimation of the stored elastic energy available to create a possible brittle fracture.

From Fig. 5 it is clear that the critical ligament thickness of densely crosslinked epoxides is very large; therefore, epoxides can be toughened to their maximum extent by adding only a small volume fraction of (preferably) non-adhering rubbery particles. However, the maximum attainable level of toughness of this class of materials is rather low compared to the low-entanglement density thermoplastic polymers (see Fig. 3).

The strain-rate and temperature dependency of the critical thickness can be modeled relatively easy via the strain-rate and temperature dependency of the yield stress, since the other parameters listed in equation (6) are relatively independent of temperature and strain-rate. In Fig. 7 the critical thickness of PS-PPE 100-0 and 20-80 w-w is shown versus strain-rate and temperature as calculated from equation (6) assuming an Eyring type of description for the strain-rate and temperature dependency of the yield stress (see ref. 9 for more details).

Fig. 7 : Critical thickness vs strain-rate and temperature for PS-PPE 100-0 and 20-80 w-w

Clearly, the value of ID_c strongly increases if the testing temperature approaches the glass transition temperature of the polymeric matrix.

CONCLUSIONS

In this work we showed that the maximum macroscopic draw ratio of core-shell-rubber modified (non-adhering to the matrix) PS-PPE blends varies from 3 (200% strain-at-break) with pure PS as a matrix ($M_c = 19.1 \text{ kg mole}^{-1}$) to about 1.6 (60% strain-at-break) if the matrix consists of PS containing 80 wt% PPE ($M_c = 5.5 \text{ kg mole}^{-1}$). For rubber-modified crosslinked epoxides, based on diglycidyl ether of bisphenol A, the maximum macroscopic draw ratio varies from 1.7 (70% strain-at-break; $M_c = 6.8 \text{ kg mole}^{-1}$) to 1.15 (15% strain-at-break; $M_c = 0.9 \text{ kg mole}^{-1}$). Remarkably, for both entangled thermoplastic polymers and crosslinked thermosets the value of the maximum macroscopic draw ratio is about 60% of the (theoretical) natural draw ratio, λ_{max} , of these polymers, independent of the nature of the network structure. Hence, the maximum macroscopic draw ratio (read: toughness) was found to scale with the square root of the molecular weight between network loci.

In order to obtain these high strain levels on a macroscopic scale, locally initiated deformation must continue without breakage of the deformed areas anywhere in the sample. For polymers of a high molecular weight between network loci (e.g. PS) the sample needs to exhibit a small characteristic length scale ($\leq 0.05 \mu\text{m}$), achieved by the introduction of non-adhering rubbery particles, in order to fulfil the conditions as described above. The value of the critical ligament thickness is a well defined function of the molecular network structure (M_c or M_e), independent of the nature of the network structure and is rather insensitive to the testing conditions applied. The values of the measured critical ligament thickness vary from $0.05 \mu\text{m}$ for PS (slow-speed tensile testing) to $0.3 \mu\text{m}$ for an epoxide having a molecular weight between crosslinks of 4.4 kg mole^{-1} .

(notched high-speed tensile testing). When the local thickness is further decreased below the critical level toughness will not increase any further. For epoxides having a molecular weight between crosslinks lower than 4 kg mole^{-1} the critical ligament thickness is larger than $0.35 \text{ }\mu\text{m}$. A simple model is presented that quantitatively describes the existence of a critical ligament thickness and its dependence on the network density, theoretical draw ratio, Young's modulus and yield stress of the macromolecular material. The strain-rate and temperature dependency of the critical thickness can be modeled via the strain-rate and temperature dependency of the yield stress.

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