Deformation and toughness of polymeric systems: 6. Critical thickness of diluted entanglement networks

M. C. M. van der Sanden* and H. E. H. Meijer†
Centre for Polymers and Composites (CPC), Eindhoven University of Technology,
PO Box 513, 5600 MB Eindhoven, The Netherlands

(Received 27 August 1993)

Following Kramer *et al.* who compared the maximum local draw ratio inside craze fibrils or shear deformation zones for different types of network structures, here the critical thickness (ID_c), below which apparently brittle amorphous glassy polymers demonstrate a macroscopic draw ratio comparable with the high values determined on a microscopic scale, is studied for two — principally different — types of physical networks. The value of ID_c is determined for network structures based on polystyrene–poly(2,6-dimethyl-1,4-phenylene ether) (PS-PPE) blends. Two types of networks are compared obtained via blending high molecular weight PPE with either (i) a (standard) high molecular weight PS (PS_h) or (ii) an extremely low molecular weight PS (PS_l). In contrast to PS_h, PS_l cannot contribute to the entanglement network structure of the blend since the molecular weight falls well below the entanglement molecular weight of PPE and, consequently, it can be considered as a (glassy) solvent for PPE. The critical thickness of two network structures with the same network density but with different values of the natural draw ratio (λ_{max}) is experimentally determined via addition of (non-adhering) core–shell rubbers. ID_c proves to be inversely proportional to the natural draw ratio of the network structure. The simple energy-based model for the prediction of ID_c quantitatively explains the differences found.

(Keywords: deformation; toughness; diluted entanglement networks)

INTRODUCTION

Following Kramer *et al.*[1–7], the phenomenon of a critical thickness (ID_c), below which brittle amorphous glassy polymers become ductile, has been extensively discussed in the previous parts of this series for thermoplastic[8–10] and thermosetting[11] polymers. Below ID_c a maximum macroscopic strain-to-break can be observed comparable with the theoretical strain-to-break of stretching the molecular (entanglement and/or crosslink) network to its full extension ($\sim \lambda_{max}$). Via an energy-based criterion[9] the absolute value of ID_c could be predicted and expressed in terms of entanglement density (ν_e) and natural draw ratio (λ_{max}):

$$ID_c = \frac{6(\gamma + k_1 \nu_e^{1/2})E_1}{\lambda_{max}\sigma_y^2} \tag{1}$$

where γ is the van der Waals surface energy, k_1 is a constant ($k_1 = 7.13 \times 10^{-15}$ J chain$^{-1/2}$ m$^{-1/2}$, ref. 9), E_1 is the Young's modulus and σ_y is the true yield stress.

In part 2[9], equation (1) is simplified by introducing the most elementary form of the network density dependency of the maximum network draw ratio: $\lambda_{max} = k_2 \nu_e^{-1/2}$, where k_2 is a constant.

A somewhat more detailed analysis of this dependency reveals that[2]:

$$\lambda_{max} = \frac{l_e}{d} \tag{2}$$

where l_e is the chain contour length and d is the entanglement mesh size while both l_e and d can be expressed in terms of entanglement density[2]:

$$l_e = \frac{\rho N_A}{M_0 \nu_e} l_0 \tag{3}$$

$$d = k_3 \left(\frac{\rho N_A}{\nu_e}\right)^{1/2} \tag{4}$$

where ρ is the density, N_A is Avogadro's number, l_0 is the length of a fully extended chain unit of molecular weight M_0 and k_3 is a constant which is polymer dependent[2]. Since equations (3) and (4) contain constants that are polymer dependent (l_0, M_0 and k_3), a given value of ν_e as measured via the plateau modulus in the melt[9] does not automatically correspond with a unique value of λ_{max}.

In this study, the validity of equation (1) will be experimentally verified using physical entanglement networks based on different types of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene ether) (PPE). PS and PPE form a homogeneously miscible system, where PPE possesses a relatively high network density,

---

* Present address: Physics Department, University of California at Santa Barbara, Broida Hall, Santa Barbara, CA 93106, USA

† To whom correspondence should be addressed

0032-3861/94/14/2991-04

$\nu_e = 13.2 \times 10^{25}$ chains m^{-3}, and PS a relatively low ν_e value (3.2×10^{25} chains m^{-3}). At the same value of ν_e, networks will be compared that consist of PPE and PS$_l$ (where PS$_l$ cannot participate in the network structure due to the fact that the molecular weight falls well below the entanglement molecular weight) with networks that are based on PPE and PS$_h$ where PS$_h$ can be part of the entanglement network structure. The previously introduced core–shell rubber (non-adhering to the PS-PPE matrix) is applied in order to set the local average ligament thickness[8].

EXPERIMENTAL

Materials

The materials used were PPE (polymerized as described in ref. 12 using toluene as a solvent), high molecular weight polydisperse PS (PS$_h$; Dow), low molecular weight PS (PS$_l$; radically polymerized) and the core–shell rubber [poly(methyl methacrylate) shell, styrene–butadiene core; Rohm and Haas Co., Paraloid EXL 3647] that was used throughout this series. The weight-average molar mass of PPE was verified with g.p.c. (CHCl$_3$; $M_w = 120$ kg mol^{-1}) and the glass transition temperature (T_g) was checked with d.s.c. [$T_g = 220$°C; i.v. $= 0.86$ dl g^{-1} (CHCl$_3$, 25°C)]. PS$_h$ was an experimental type containing no additives with a $T_g = 100$°C (d.s.c.) and a $M_w = 200$ kg mol^{-1} (g.p.c.: CHCl$_3$). The PS$_l$ was prepared according to the method described by Rempp and Merrill[12] (80°C) and subsequently characterized by g.p.c. [$M_w = 3.5$ kg mol^{-1}, well below the entanglement molecular weight of both PS$_h$ (19.1 kg mol^{-1})[5,9] and PPE (4.5 kg mol^{-1})[5,9]] and d.s.c. ($T_g = 80$°C).

Sample preparation

Two series of PS$_h$-PPE and PS$_l$-PPE blends containing different amounts of core–shell rubbers (0–60 wt%) were prepared by casting mixtures of the three polymeric components dissolved in chloroform (10 wt% solutions). Subsequently, the films (with a final average thickness of 0.3 mm) were dried under vacuum conditions at a temperature of 100°C for 48 h. Small dumb-bell shaped tensile specimens were machined from the films according to ASTM D 1708.

Scanning electron microscopy (SEM)

SEM (Cambridge Stereo Scan 200) was carried out in order to check the rubber particle distribution in the prepared PS-PPE blends. Specimens were prepared by fracturing the samples at liquid-nitrogen temperature. Subsequently, the samples were coated with a conducting gold layer.

Mechanical testing

Slow-speed tensile testing was performed on a Frank tensile machine (type 81565) at a cross-head speed of 5 mm min^{-1} at room temperature. All measurements were carried out five times.

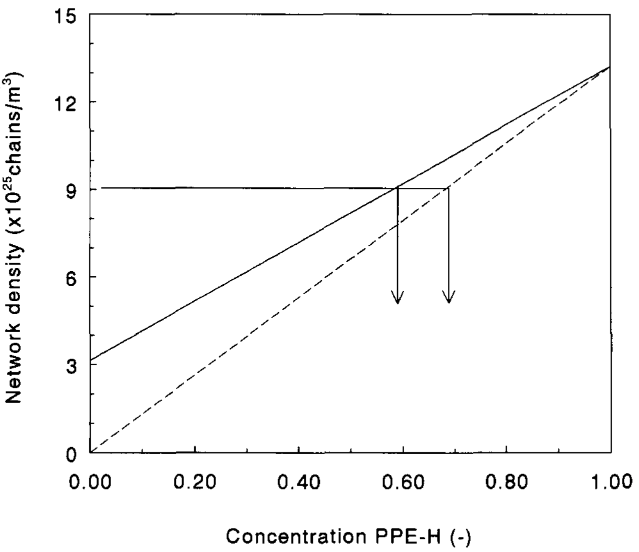

Figure 1 Network density *versus* concentration PPE for PS$_h$-PPE and PS$_l$-PPE blends. For details, see text

RESULTS AND DISCUSSION

Network density and natural draw ratio

In order to compare rubber-modified blends based on PS$_h$-PPE with blends having a PS$_l$-PPE matrix at the same entanglement density, the correlation between network density and concentration PPE must be determined for both dilution methods. The experimental determination of the network density of blends based on PS$_h$ and PPE has already been described in part 2 of this series[9]. Prest and Porter[13] have derived an empirical relationship between the weight fraction of PPE (χ) in the PS$_h$-PPE blend and the network density of the miscible blend:

$$\nu_e(\chi) = \nu_{e(PS)}(1 + 3.2\chi) \tag{5}$$

where $\nu_{e(PS)}$ is the network density of PS$_h$ (3.2×10^{25} chains m^{-3}, ref. 9). This correlation is illustrated in *Figure 1* (solid line). If the entanglement network of PPE is diluted by the addition of PS$_l$, the latter component cannot participate in the entanglement network since the molecular weight is lower than the entanglement molecular weight of neat PPE (4.5 kg mol^{-1}). Hence, the entanglement density of the blend can simply be described as:

$$\nu_e(\chi) = \chi \nu_{e(\chi=1)} \tag{6}$$

where $\nu_{e(\chi=1)}$ is the network density of neat PPE (13.2×10^{25} chains m^{-3}). The value of ν_e as a function of the concentration of PPE ($=\chi$) is shown in *Figure 1* for the PS$_l$-PPE blend (broken line).

As already demonstrated by Donald and Kramer[5], the value of the natural draw ratio of a PS-PPE blend does not only depend on the network density of the system but also on the 'dilution method'. Therefore, it is interesting to compare the values of λ_{max} of the PS$_h$-PPE system with the values of λ_{max} of PS$_l$-PPE blends as a function of the concentration of PPE (i.e. χ). For both types of blends values of $\lambda_{max}(\chi)$ can be obtained from data reported by Donald and Kramer[5] using equations (2), (3) and (4) where the corresponding values of ν_e can be obtained from equations (5) and (6). In *Figure 2* the $\lambda_{max}(\chi)$ values extracted from the literature data are shown for both types of blends: the solid curve corresponds to the PS$_h$-PPE blends, the broken curve represents the ν_e-dependency of the natural draw ratio for the PS$_l$-PPE system.

For two different blends possessing the same network density (9×10^{25} chains m^{-3}, chosen arbitrarily but within the realizable range) but with a different value of λ_{max},

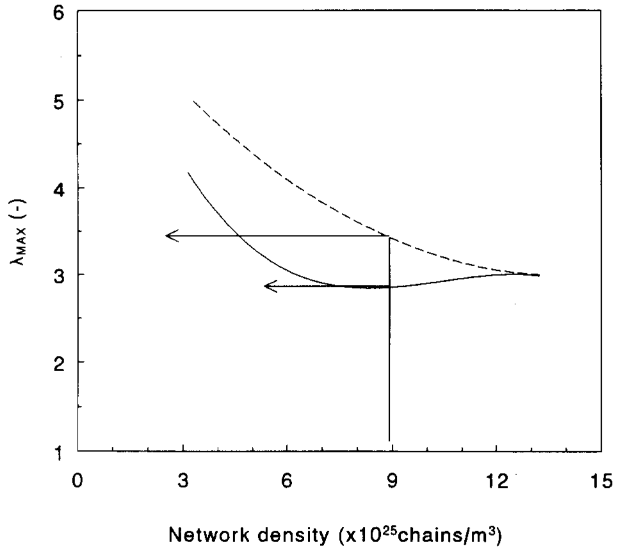

Figure 2 Natural draw ratio *versus* network density for PS_h-PPE and PS_l-PPE blends. For details, see text

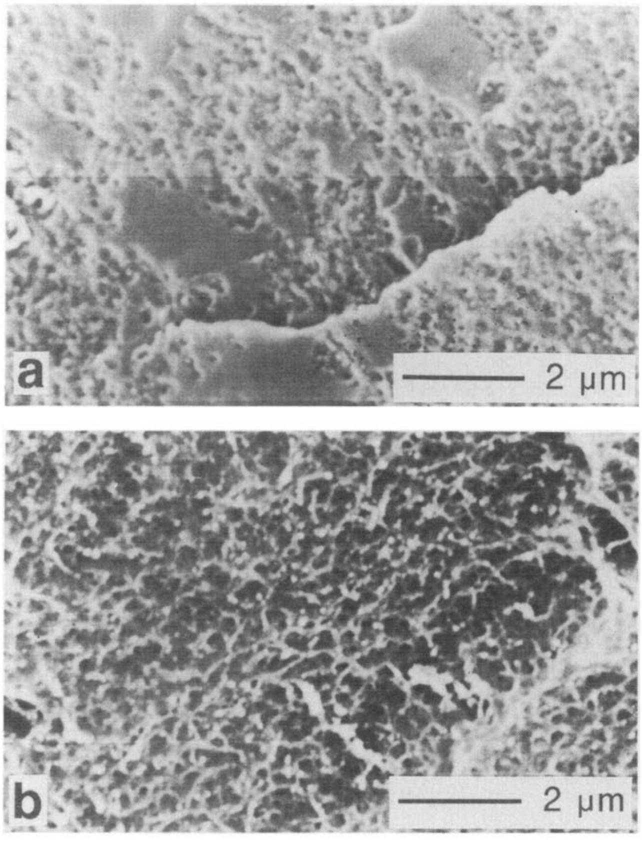

Figure 3 SEM micrographs of (a) a 40 wt% core–shell rubber-modified PS_h-PPE 40-60 blend and (b) a 60 wt% core–shell rubber-modified PS_l-PPE 30-70 blend

the critical thickness is determined and verified with equation (1). The blend compositions corresponding to this network density of 9×10^{25} chains m^{-3} can be determined from *Figure 1* and results in PS_h-PPE 40-60 and PS_l-PPE 30-70. The corresponding values of λ_{max} are 2.9 and 3.5, respectively (*Figure 2*).

Before mechanical analysis the homogeneity of the spatial rubber particle distribution for both types of core–shell rubber-modified PS-PPE blends is verified (*Figure 3*). For both dilution methods the rubber particle distribution proves to be rather homogeneous, independent of the rubber concentration.

Slow-speed tensile testing

The critical thickness of PS-PPE blends is indicated by a sudden increase in strain-to-break on a macroscopic scale for slow-speed uniaxial tensile testing[8]. In *Figure 4* the macroscopic strain-to-break of the two blends is demonstrated as a function of the rubber concentration. For the PS_h-PPE 40-60 blend a sudden increase in strain-to-break is observed at a rubber concentration of 20 wt%. Assuming a body-centred-cubic lattice[8] for the spatial rubber particle distribution the critical average surface-to-surface interparticle distance (ID_c) can be calculated from the critical rubber concentration (20 wt%) and average rubber particle size (i.e. 0.2 μm) and equals 0.15 μm. As expected, this value agrees well with the value of ID_c already reported in part 2 of this series[9] for the extruded PS-PPE 40-60 blend ($ID_c=0.18$ μm). However, for the PPE network diluted by the addition of PS_l the brittle-to-ductile transition occurs at a significantly higher rubber concentration (35 wt%), i.e. a lower value of ID_c (0.09 μm). In *Table 1* the values of ID_c as predicted by the energy-based model [equation (1), using $\gamma=40\,mJ\,m^{-2}$ (ref. 2) and assuming a constant yield stress of 70 MPa and a Young's modulus of 3 GPa] are listed for both PS_h-PPE 40-60 and PS_l-PPE 30-70 blends and compared with the experimentally determined values. Clearly, the model predictions show not only a qualitative but

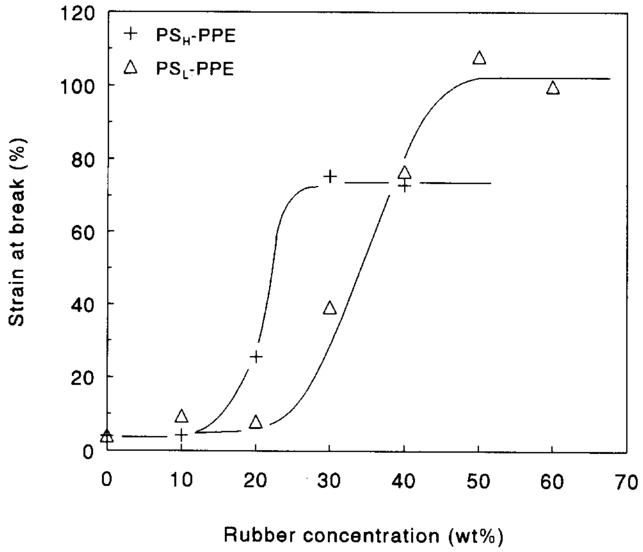

Figure 4 Strain-to-break of core–shell rubber-modified PS_h-PPE 40-60 and PS_l-PPE 30-70 blends

Table 1 Predicted and experimental values of ID_c and the macroscopic draw ratio for PS-PPE blends ($v_e=9\times10^{25}$ chains m^{-3})

Blend composition	ID_c (model) (μm)	ID_c (exp.) (μm)	0.6 λ_{max}	λ_{macr}
PS_h-PPE 40-60	0.14	0.15	1.74	1.75
PS_l-PPE 30-70	0.11	0.09	2.1	2

also a quantitative agreement with the experimentally determined values of ID_c.

The macroscopic strain-to-break in the ductile region (λ_{macr}), below the critical thickness, has been demonstrated to correlate with the natural draw ratio by $\lambda_{macr} = 0.6\ \lambda_{max}$ (refs 8, 9 and 11). In *Table 1* the values of λ_{macr} and of $0.6\lambda_{max}$ are listed. These data clearly confirm the previously found relationship between the macroscopic maximum draw ratio and the molecular network structure.

CONCLUSIONS

Two different dilution methods of a high molecular weight PPE entanglement network are compared. The critical thicknesses (below which polymers become macroscopically tough) of PS_h-PPE 40-60 and PS_l-PPE 30-70 blends, with a constant network density of 9×10^{25} chains m^{-3} but with different values of the natural draw ratio (2.9 and 3.5, respectively), have been experimentally determined to be 0.15 and 0.09 μm, respectively. The energy-based criterion for the explanation of the phenomenon of the critical thickness as introduced in part 2 of this series[9] results in a satisfying quantitative agreement with the experimentally determined values of ID_c. The values of the maximum macroscopic strain correspond to the maximum network strain in a similar way as found for all polymer systems previously studied within this series ($\lambda_{macr}/\lambda_{max} = 0.6$).

ACKNOWLEDGEMENTS

The authors kindly wish to thank B. Th. de Jong, P. P. Koets and H. H. P. Moonen for the synthesis and characterization of the various polymers and for performing the mechanical analysis of the rubber-modified systems. The General Electric Co. is acknowledged for the determination of the molecular weight of the synthesized PPE and P. Vollenberg of Dow Benelux NV is acknowledged for supplying the PS_h. This work was sponsored by the Foundation for Polymer Blends (SPB).

REFERENCES

1 Kramer, E. J. *Adv. Polym. Sci.* 1983, **52/53**, 1
2 Kramer, E. J. and Berger, L. L. *Adv. Polym. Sci.* 1990, **91/92**, 1
3 Henkee, C. and Kramer, E. J. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 721
4 Donald, A. M. and Kramer, E. J. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 899
5 Donald, A. M. and Kramer, E. J. *Polymer* 1982, **23**, 461
6 Donald, A. M. and Kramer, E. J. *Polymer* 1982, **23**, 1183
7 Glad, M. D. and Kramer, E. J. *J. Mater. Sci.* 1991, **26**, 2273
8 Van der Sanden, M. C. M., Meijer, H. E. H. and Lemstra, P. J. *Polymer* 1993, **34**, 2148
9 Van der Sanden, M. C. M., Meijer, H. E. H. and Tervoort, T. A. *Polymer* 1993, **34**, 2961
10 Van der Sanden, M. C. M. and Meijer, H. E. H. *Polymer* 1994, **35**, 2774
11 Van der Sanden, M. C. M. and Meijer, H. E. H. *Polymer* 1993, **34**, 5063
12 Rempp, P. and Merrill, E. W. 'Polymer Synthesis', Huethig and Wepf Verlag, Basel, 1986
13 Prest, W. M. and Porter, R. S. *J. Polym. Sci. A2* 1972, **10**, 1639