Toughness enhancement in amorphous polymers

Toughness Enhancement in Amorphous Polymers

I.A. van Casteren, J.G.P. Goossens, H.E.H. Meijer

Eindhoven University of Technology,
Faculty of Mechanical Engineering,
Section Materials Technology,
P.O. Box 513, 5600 MB Eindhoven, the Netherlands

Introduction

The brittleness of amorphous polymers like polystyrene (PS) and poly(methyl metacrylate) PMMA is the result of extreme strain localisation in the form of crazes. Delocalisation of the local strain will transfer the high intrinsic ductility to a macroscopic level and can be used to toughen PS. The maximum toughness is expected for an easily cavitating nanosized modifier, which supports the strain hardening process at higher strains[1,2](figure 1).

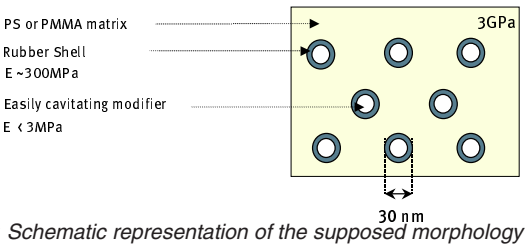

Figure 1: Schematic representation of the supposed morphology

A possible route to prepare a system which meets these requirements may be the application of diblock copolymer micelles[3]. These molecular structures should be formed in a reactive solvent, like styrene or MMA, which after polymerisation forms the continuous phase.

Results

Poly(ethylene oxide) and polybutadiene macroinitiators have been used for the synthesis of acrylates-based diblocks by Atom Transfer Radical Polymerisation (ATRP)(figure 2).

$$\begin{array}{ccc} PB-Cl+Cu^{I}L_2 & \overrightarrow{\longleftarrow} & PB\cdot+Cu^{II}L_2Cl \\ & & \downarrow +Monomer(M) \\ PBM_x-Cl+Cu^{I}L_2 & \overrightarrow{\longleftarrow} & PBM_x\cdot+Cu^{II}L_2Cl \end{array}$$

Figure 2: Reaction mechanism of Atom Transfer Radical Polymerisation with PB-CL=chloride-end functionalised polybutadiene, L=PMDETA

The synthesised diblocks have been analysed by H-NMR, SEC and SAXS. The peak positions in SAXS suggest a cylindrical morphology(figure 3).

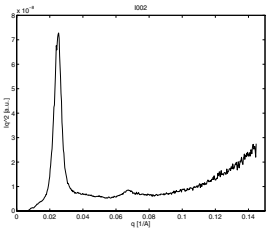

Figure 3: Pure PB-PBA

The morphology development during polymerisation of MMA solutions containing various diblock copolymers has been studied by SAXS and Raman spectroscopy as a function of amount of initiator, polymerisation temperature and diblock copolymer concentration.

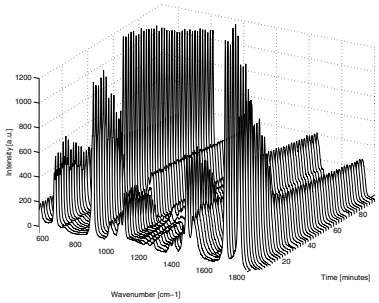

Figure 4: Raman spectra of the polymerisation of MMA with 5% PB-PBA, T=100° C. Changes in peak intensities are used to quantify the conversion as a function of time (C=C at 1635 cm^{-1}) and conclusions can be drawn about reorganisation of the diblock.

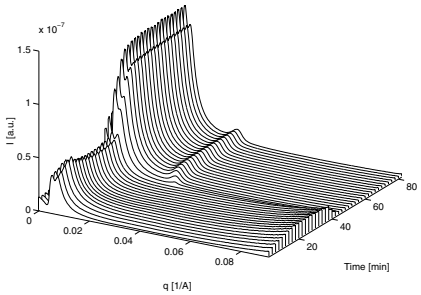

Figure 5: Time Resolved Small Angle X-ray Scattering spectra of the polymerisation of MMA with 5% PB-PBA, T=100° C, increased intensities around the beamstop may indicate macrophase separation.

Conclusions

- SAXS and Raman spectroscopy can be used to follow the morphology during polymerisation
- Controlled polymerisation conditions are necessary to avoid macrophase separation

Future Work

- Visualisation of final morphology by various microscopy techniques
- Studying the mechanical properties
- Introduction of hydrogen bonds to avoid macrophase separation

References:

[1] SMIT, R.J.M.,*Ph.D. thesis*, EINDHOVEN, UNIVERSITY OF TECHNOLOGY, 1998 :

[2] JANSEN, B.J.P., *Ph.D. thesis*, EINDHOVEN, UNIVERSITY OF TECHNOLOGY, 1998

[3] BATES ET AL.,*J.Am. Chem. Soc.*, 1997, 2749