ELSEVIER

Real-time SANS study of interpenetrating polymer network (IPN) formation

Robert P. Burford[a],*, Martin G. Markotsis[a], Robert B. Knott[b]

[a]*School of Chemical Engineering and Industrial Chemistry, CRC for Polymers, University of New South Wales, NSW 2052, Australia*
[b]*Australian Nuclear Science and Technology Organisation, Private Mail Bag, Menai, NSW 2234, Australia*

Abstract

Interpenetrating polymer networks (IPNs) are a combination of two or more polymers in network form, with at least one polymer polymerised and/or crosslinked. The nanostructure was investigated for sequential IPNs formed from (i) either radial or linear poly(styrene-co-butadiene-co-styrene) (SB_4/SBS) copolymer, and (ii) polystyrene (PS). For polymer network I, the SB_4/SBS copolymer self-assembled into ordered micro-domain structures, which acted as a template for the resultant IPN. The formation of the IPN was studied using real-time small angle neutron scattering. For the linear SBS IPN, the time-zero pattern showed an ordered lamella structure and as polymerisation and crosslinking progressed, the first-order peak increased in amplitude (factor $\times 4$) and higher-order peaks appeared. The position and width of the first-order peak did not change significantly, indicating that the size and spacing of the domains did not change. The increase in molecular organisation can be attributed to (i) sharpening of phase boundaries, (ii) annealing of domain positions, and/or (iii) increasing the contrast by material moving between domains. Investigations of phase transformation kinetics may aid in the design of specific structures for nanotechnology applications, as well as traditional engineering applications.
Crown Copyright © 2006 Published by Elsevier B.V. All rights reserved.

PACS: 61.12.Ex; 81.05.Lg; 82.35.Jk

Keywords: Interpenetrating polymer networks; Sans; Real-time network; Thermoplastic elastomers

1. Introduction

Interpenetrating polymer networks (IPNs) are a combination of two or more polymers in network form, with at least one polymer network polymerised and/or crosslinked in the presence of the other(s) [1]. Whilst molecular interpenetration is an ultimate goal of IPN formation, it is generally accepted that most IPNs do not interpenetrate on a molecular scale, however they may form phase regions of the order of tens of nanometres [2].

In this study, sequential IPNs were investigated where polymer network I was formed by thermal cross-linking, followed by the formation of network II. IPNs with both networks cross-linked are full-IPNs, and with only network I cross-linked are semi-IPNs. Two full- and two semi-IPNs were studied to investigate the effect of cross-linking of

network II on the IPN domain structure. IPNs using thermoplastic elastomers (TPEs) as starting materials form tough strong composites when the nanostructure is controlled. Since block copolymers self assemble into a range of morphologies [3] (spheres, cylinders and lamella), these highly ordered structures can be used to give IPNs unique thermal and mechanical properties. The TPEs selected were block copolymers of poly(styrene-co-buta-diene-co-styrene) (SB_4 and SBS) [4]. Earlier work showed that the styrene (network II) preferentially migrated into the polystyrene (PS) phase domains (SB_4/SBS network I) thus forming the IPN within the SB_4/SBS structure [5].

The small angle neutron scattering (SANS) technique is ideal for investigating block copolymer morphology [6], and particularly to investigate cross-linking reactions in polymer blends [7,8]. SANS provides unique information on the structural organization of IPNs especially when deuterium labelling is used [9,10]. In this study, however, the scattering length densities of the (poly)butadiene (PB)

*Corresponding author. Tel.: +61 2 9385 4308; fax: +61 2 9385 5966.
E-mail address: r.burford@unsw.edu.au (R.P. Burford).

$(-0.46 \times 10^6 \,\text{Å}^{-2})$, and PS $(1.42 \times 10^6 \,\text{Å}^{-2})$ provided adequate contrast without the need for deuteration. In fact, the contrast was sufficient for real-time observation of kinetic effects on the 5–10 min time scale.

The SANS technique is a powerful technique. However, it should not be used in isolation. In related studies, a range of techniques, including TEM, AFM, SAXS and SANS was used to investigate the structure/property relationships of PS/SB$_4$/SBS IPNs with 70% total PS content [11–13].

2. Materials

Two grades of SB$_4$/SBS block copolymers (Kraton^{TM} D1101 and D1184) (Toyota Tsusho, Australasia, Pty Ltd.) were used as received (Table 1).

Dicumyl peroxide (Dicup^{TM}) (BF Specialty Chemicals) was used without further purification to cross-link the SB$_4$/SBS. The stabilisers in styrene monomer (Nuplex Industries Pty Ltd.) were removed using a column of basic alumina. The initiator, benzoyl peroxide (BPO) (Laporte Organics), and cross-linker, divinyl-benzene (DVB) (Aldrich), were used without further purification.

Table 1
Properties of SB$_4$/SBS block copolymers

	Kraton^{TM} D1101	Kraton^{TM} D1184
Styrene/butadiene ratio	29/71	30/70
Molecular weight	104,000	208,000
Polydispersity	~1.1	~1.3
Molecular structure	Linear SBS	Radial SB$_4$
Solid-state structure	Lamella	?

3. Experimental

Linear SBS or radial SB$_4$ was mixed with Dicup^{TM} in a rotary mixer at 90 °C for 5 min and thermally cross-linked at 140 °C and 276 kPa for 30 min. Samples $\sim 40 \times 20 \times 1 \, \text{mm}^3$ were cut from the pressed sheets. Styrene monomer, BPO initiator and DVB crosslinker were added to one cross-linked pad of (i) linear SBS, and (ii) radial SB$_4$, to form full-IPNs. The semi-IPNs were formed by adding only styrene monomer and BPO. The total styrene content was 70% which is the optimum ratio for combining stiffness with toughness [14]. Once the styrene had been absorbed, the pads were placed (in turn) in a temperature-controlled cell at 90 °C on the 8 m SANS instrument at the NIST Centre for Neutron Research (NCNR Gaithersburg USA) [15]. This instrument used a 6 Å neutron wavelength beam with a detector offset angle of 0°. The beam source aperture was 12.5 mm with a sample aperture of 6.7 mm and a 25 mm beam stop to obtain a minimum scattering vector q of $\sim 0.006 \,\text{Å}^{-1}$ (where $q = (4\pi/\lambda)\sin(\theta/2)$, λ is the neutron wavelength and θ the scattering angle). SANS data was collected in 5 min intervals for ~ 120 min.

The scattering intensity $I(q)$ was corrected for electronic background, sample transmission and thickness, empty-cell scattering, and detector inhomogeneity; and placed on an absolute scale using a secondary standard. The 2D patterns were sector averaged with half-sector angle of 45° around the major axis. The data was reduced using IGOR software (Wavemetrics Inc. USA).

4. Results and discussion

SANS studies of PS/SB$_4$/SBS IPNs confirmed that the structure of the self-assembled SB$_4$/SBS precursor acted as a template for the IPN [11]. This is most clearly seen in the
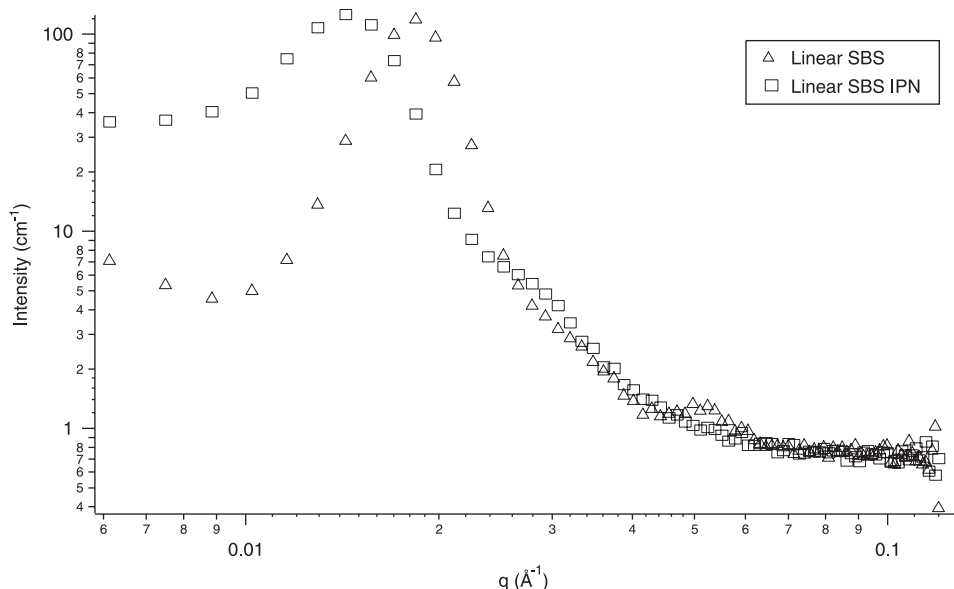

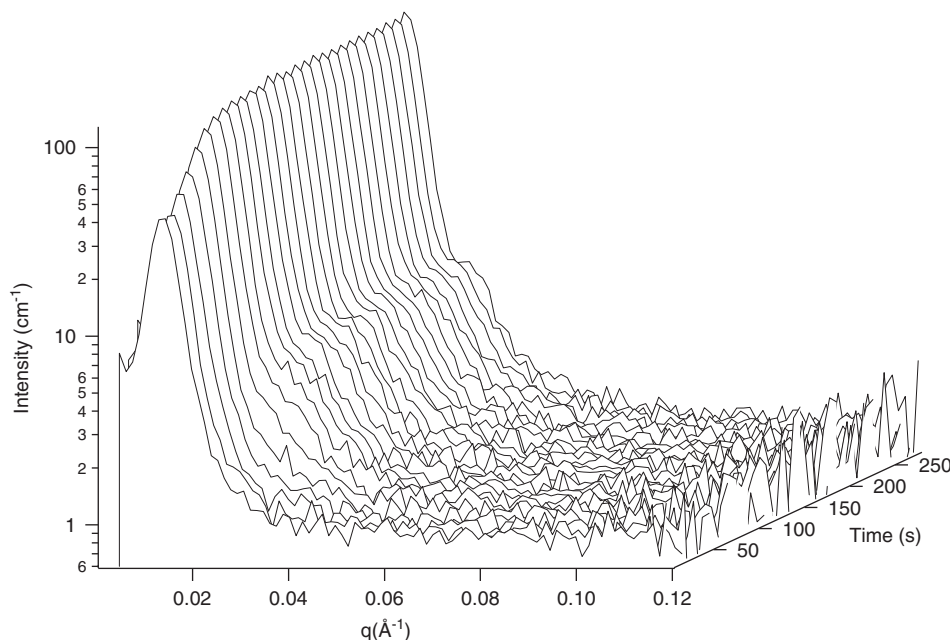Fig. 1. 1D SANS profiles for linear SBS and a linear SBS IPN.

Fig. 2. Time-resolved 1D SANS profiles for a linear SBS IPN.

linear SBS IPN. The 1D SANS profiles (Fig. 1) show the IPN peak at lower q than the SBS starting material, indicating that the PS domains swell with added styrene.

The time-resolved SANS experiments provided insight into PS network II formation. The four samples studied showed a general increase in order with time, and the most noteable example is the linear SBS full-IPN (Fig. 2). The 1D SANS profiles initially showed the same highly ordered structure as the static SANS studies (lamellar or cylindrical morphology). As polymerization and cross-linking progressed, a second-order peak appeared at ~45–50 min, and after ~75 min a third diffraction peak was visible. Generally, the 1D SANS profiles of the radial SB_4 IPNs showed broader peaks than the linear SBS IPNs. The formation of semi-IPNs also showed an increase in order as shown by the appearance of a second diffraction peak.

Fig. 3 is a plot of the maximum amplitude of the first-order peak as a function of time, and clearly shows the approach to equilibrium for all samples except the radial SB_4 full-IPN. (This experiment was terminated due to equipment failure). The increase in order is attributed to (i) sharpening of phase boundaries, (ii) annealing of domain positions, and/or (iii) increasing the contrast by material moving between domains. The increase in order is consistent with the hypothesis that there was styrene monomer in the bulk PB and in the phase boundaries between PS and PB regions of the SB_4/SBS, which, as the polymerization reaction proceeded, concentrated in the styrene domains and the newly forming styrene network. As an indication of the magnitude of this effect, a ~10 wt% initial concentration of PS in the PB domain would lead to a ~25% increase in $I_{max}(q)$ which is not sufficient to completely account for the observed increase. As the concentration of styrene in the PB regions decreased, and
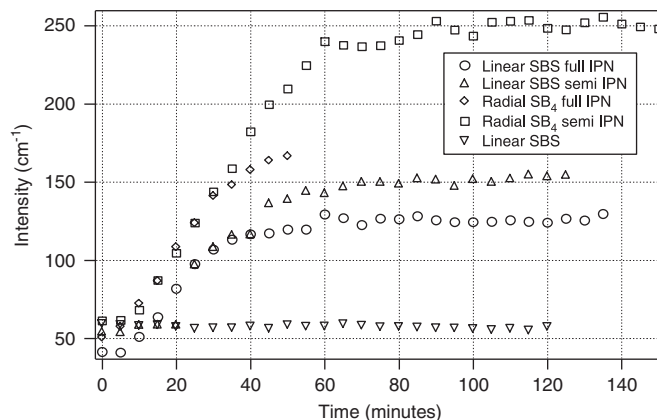

Fig. 3. Maximum intensity of the first order peak as a function of time at 90 °C.

the phase boundaries became sharper and more distinct, the neutron contrast between the PB and PS phases increased.

To determine if the observed changes were occurring in the SB_4/SBS independently of the added styrene network, a linear SBS pad soaked in d_8-toluene was studied. As shown in Fig. 3, there was no change in the size or shape of the SBS network, thereby indicating that the observed changes in IPN morphology were primarily due to the movement and development of the PS network II.

5. Conclusion

SANS was used to examine the formation of bulk nanostructure in IPN materials as network II formed in the presence of the network I. As the styrene network II forms,

an increase in the long-range order can be observed. The strong diffraction patterns obtained with the linear SBS IPNs indicate the formation of distinct phase domains with sharp boundaries within the highly oriented morphology. The radial SB$_4$ IPNs are less ordered, reflecting the greater steric hinderance of the radial polymer chains.

Acknowledgements

References

[1] L.H. Sperling, V. Mishra, in: S.C. Kim, L.H. Sperling (Eds.), IPNs Around the World, Wiley, Chichester, 1997.

[2] L.H. Sperling, in: D. Klempner, L.H. Sperling, L.A. Utracki (Eds.), Interpenetrating Polymer Networks, American Chemical Society, Washington, DC, 1994.

[3] A.J. Ryan, I.W. Hamley, in: R.N. Haward, R.J. Young (Eds.), Physics of Glassy Polymers, Chapman & Hall, London, 1997.

[4] L. Zhu, B.H. Calhoun, Q. Ge, R.P. Quirk, S.Z.D. Cheng, E.L. Thomas, B.S. Hsiao, F. Yeh, L. Liu, B. Lotz. Macromol. 34 (2001) 1244.

[5] J.J. Jones, R.P. Burford, Polym. Inter. 26 (1991) 163.

[6] P. Cebe, in: P. Cebe, B.S. Hsiao, D.J. Lohse (Eds.), Scattering from Polymers: Characterisation by X-rays, Neutrons, and Light, American Chemical Society, Washington, DC, 2000, pp. 2–22.

[7] Q. Tran-Cong, in: T. Araki, Q. Tran-Cong, M. Shibayama (Eds.), Structure and Properties of Multiphase Polymeric Materials, Marcel Dekker, New York, 1998, pp. 67–120.

[8] B. Hammouda, Adv. Polym. Sci. 106 (87) (1993) 89.

[9] R.W. Richards, in: Die Makromolekulare Chemie, Macromolecular Symposia, 1990, Huthig & Wepf Verlag, Basel, Heidelberg, New York, Jerusalem.

[10] J. Lal, J.M. Widmaier, J. Bastide, F. Boué, Macromolecules 27 (1994) 6443.

[11] M.G. Markotsis, Ph.D. Thesis. University of NSW, 2005.

[12] R.P. Burford, M.G. Markotsis, R.B. Knott, Nucl. Instr. and Meth. B 208 (2003) 58.

[13] R.P. Burford, J.J. Jones, in: Progress in Pacific Polymer Science, vol. 2, Springer, Berlin, 1992.

[14] K.T. Tan, University of NSW, B.Sc. Honours Thesis, 1998.

[15] B. Hammouda, S. Krueger, C.J. Glinka, J. Res. Nat. Inst. Stand. Technol. 98 (1993) 31.