

Microcrystalline parameters of polyurethane/polymethyl methacrylate semi interpenetrating polymer networks by WAXS

H. Kumar^a, Siddaramaiah^{b,*}, R. Somashekar^c, S.S. Mahesh^c

^a Department of Chemistry, R.V. College of Engineering, Mysore Road, Bangalore, Karnataka 560059, India

^b Department of Polymer Science & Technology, Sri Jayachamarajendra College of Engineering, Mysore 570006, India

^c Department of Studies in Physics, University of Mysore, Mysore 570006, India

Received 14 May 2006; received in revised form 5 August 2006; accepted 12 October 2006

Abstract

A series of polyurethane (PU) and polymethyl methacrylate (PMMA) semi interpenetrating polymer networks (SIPNs) in the weight percent ratios of 90/10, 70/30, 60/40 and 50/50 were synthesized. The obtained SIPNs were characterized for physico-mechanical properties. Wide angle X-ray scattering studies (WAXS) were made to know microcrystalline parameters such as crystal size ($\langle N \rangle$), lattice disorder (g), surface (D_s) and volume (D_v) weighted crystal size of SIPNs. These parameters were expressed using exponential, lognormal and Reinhold asymmetric column length distribution functions and results are compared.

© 2006 Elsevier B.V. All rights reserved.

Keywords: IPNs; X-ray; Models; Microcrystalline parameters; Lattice disorder; Distribution functions

1. Introduction

The field of polyurethane (PU) and its interpenetrating polymer networks (IPNs) have become important area of research in recent years. Polyurethanes with different polyols and diisocyanates have been prepared and characterized by many scientists [1–9]. IPNs made with elastomeric PU and rigid plastic of some sort, polymethyl methacrylate (PMMA) or polystyrene (PS) are most popular [1]. Castor oil based PU and PS IPNs have been investigated by many researchers [2–6]. These studies revealed the transition from stress–strain behaviour of reinforced elastomers to toughened plastics. Jordhamo et al. [6] studied the phase inversion with different amount of PS and PU with different amounts of cross linker divinyl benzene (DVB). Castor oil and methylene diisocyanate (MDI) based PU/PS IPNs were studied by Ku et al. [7]. They have found that phase inversion occurs with 20–30% PU in PU/PS IPNs.

Many researchers have studied the X-ray scattering of polymethyl methacrylate blends and IPNs [8–13]. In our earlier communications, we have reported the WAXS studies on PU and its IPNs with PS and PAN [14–17]. Few literature are avail-

able on IPNs of PU/PMMA is for different PU system [18,19]. Hence, there is lack of literature on polyethylene glycol based PU/PMMA IPNs microcrystalline parameters. The present study is an effort to interpret observed physico-chemical properties of PU/PMMA IPNs with X-ray technique and using three different models such as exponential, lognormal and Reinhold asymmetric column length distribution functions. Each of the Bragg reflections in these samples, referred as (hkl) reflections, are broadened due to crystal imperfections, we have used line profile analysis technique to quantify these imperfections. Normally, the broadening of a profile arises due to limited number of unit cells called crystal size ($\langle N \rangle$), counted in a direction perpendicular to Bragg planes (hkl) and a disorder of second kind, referred as lattice strain (g in %). This is given by $\Delta d/d$, where d is the interplanar spacing and Δd is the change in interplanar spacing.

2. Experimental

2.1. Materials

Polyethylene glycol-400 (PEG) (M/s. Ranbaxy Laboratories, India), benzoyl peroxide (Aldrich, USA) and 4,4'-diphenyl methane diisocyanate (MDI) (Merck, USA) were used as such.

* Corresponding authors. Tel.: +91 821 2512568; fax: +91 821 2515770.
E-mail address: siddaramaiah@yahoo.com (Siddaramaiah).

Methyl methacrylate (s d Fine Chem Ltd., Boisor, India) monomer was freed from stabilizer prior to use.

2.2. Procedure

Polyethylene glycol-400 and 4,4'-diphenyl methane diisocyanate (MDI) based polyurethane was prepared using a new catalyst (0.05%) as reported elsewhere [20] by sequential polymerization method [14,21]. The PU was prepared by reacting hydroxyl groups of macro diol, PEG with MDI in the molar ratio of 1:1.5. The methyl methacrylate monomers trapped in PU have been subsequently polymerized by radical polymerization using 0.5% benzoyl peroxide. The reaction mixture was stirred thoroughly at room temperature for 30 min to get homogeneous solution. The solution was poured into a cleaned glass mould sprayed with releasing agent. The mould was kept at room temperature for 24 h for PU polymerization. The temperature of the mould was then slowly raised to 80 °C to initiate polymerization of methyl methacrylate monomer and maintained for 12 h. The obtained transparent light yellow PU/PMMA IPNs with different compositions were cooled slowly and taken out from the mould.

2.3. Techniques

2.3.1. Physico-mechanical behaviour

Mechanical properties like tensile strength and percentage elongation at break were measured as per ASTM D-882 method using Hounsfield Universal testing machine (UTM, UK) H50 KM, 50 KN. A minimum of six samples were tested for each composition and the average value has been reported. The surface hardness of the IPNs was measured using durometer as per ASTM D 785 method.

2.3.2. X-ray powder pattern recording and analysis

X-ray powder pattern of IPNs were recorded using Philips PW 1140 diffractometer of Bragg-Branto Geometry (fine focus setting) with germanium monochromatic radiation of Cu K α ($\lambda = 0.1542$ nm) for 2θ range 5–50 at intervals of 0.03 employing a curved position sensitive detector (CPSD) in the transmission mode. These patterns were indexed using TREOR procedure. The intensity was corrected for Lorentz-polarization factors and also for instrumental broadening using Stokes deconvolution method [22].

Microstructural parameters like crystal size ($\langle N \rangle$) and lattice strain (g in %) were usually determined by employing Fourier method reported elsewhere [23–25]. The intensity of a profile in the direction joining the origin to the center of the reflection can be expanded in terms of Fourier cosine series:

$$I(s) = \sum_{n=-\infty}^{\infty} A(n) \cos\{2\pi nd(s - s_0)\} \quad (1)$$

where the coefficients of the harmonics $A(n)$ are functions of the size of the crystallite and the disorder of the lattice. Here, s is $\sin(\theta)/(\lambda)$, s_0 the value of s at peak of a profile, n the harmonic order of coefficient and d is the lattice spacing. The Fourier

coefficients can be expressed as:

$$A(n) = A_s(n) \cdot A_d(n) \quad (2)$$

For a paracrystalline material, $A_d(n)$ can be obtained, with Gaussian strain distribution [25,26]:

$$A_d(n) = \exp(-2\pi^2 m^2 n g^2) \quad (3)$$

here ' m ' is the order of the reflection and $g = (\Delta d/d)$ is the lattice strain. Normally one also defines mean square strain ($\langle \varepsilon^2 \rangle$), which is given by g^2/n . This mean square strain is dependent only on n , but not g [27,28]. For a probability distribution of column lengths $P(i)$, we have:

$$A_s(n) = 1 - \frac{nd}{D} - \frac{d}{D} \left[\int_0^n i P(n) di - n \int_0^n P(i) di \right] \quad (4)$$

where $D = \langle N \rangle d_{hkl}$ is the crystallite size and ' i ' is the number of unit cells in a column. In the presence of two orders of reflections from the same set of Bragg planes, Warren and Averbach [23] have shown a method of obtaining the crystal size ($\langle N \rangle$) and lattice strain (g in %). But in polymers very rarely, we find multiple reflections. So, to find the finer details of microstructure, we approximate the size profiles by simple analytical function for $P(i)$ by considering only the asymmetric functions. Another advantage of this method is that the distribution function is different along different directions. Generally single crystal size distribution function is used for the whole pattern fitting, but we feel, it may be inadequate to describe polymer diffraction patterns [27–29]. Hence, it is emphasized that the Fourier method of profile analysis (single order method used here) is quite reliable one as per the recent survey and results of Round Robin test conducted by IUCr [30]. In fact for refinement, we have also considered the effect of background by introducing a parameter [31].

2.3.3. The exponential distribution

It is assumed that there are no columns containing fewer than p unit cells and those with more decay exponentially. Thus, we have [32],

$$P(i) = \begin{cases} 0; & \text{if } p < i \\ \alpha \exp\{-\alpha(i - p)\}; & \text{if } p \geq i \end{cases} \quad (5)$$

where $\alpha = 1/(N - p)$.

Substituting this in Eq. (4), we get:

$$A_s(n) = \begin{cases} A(0)(1 - n/\langle N \rangle); & \text{if } n \leq p \\ A(0)\{\exp[-\alpha(n - p)]\}/(\alpha N); & \text{if } n \geq p \end{cases} \quad (6)$$

Here ' α ' is the width of the distribution function, ' i ' the number of unit cells in a column, ' n ' the harmonic number, ' p ' the smallest number of unit cells in a column and $\langle N \rangle$ is the number of unit cells counted in a direction perpendicular to the (hkl) Bragg plane.

Download English Version:

<https://daneshyari.com/en/article/1584339>

Download Persian Version:

<https://daneshyari.com/article/1584339>

[Daneshyari.com](https://daneshyari.com)