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Effects of organophilic montmorillonite on hydrogen bonding, free volume and glass transition temperature of epoxy resin/polyurethane interpenetrating polymer networks ☆

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Abstract

Epoxy resin nanocomposites containing organophilic montmorillonite (oM) and polyurethane were prepared by adding oM to interpenetrating polymer networks (IPNs) of epoxy resin and polyurethane (EP/PU). The dispersion degree of oM in EP/PU matrix was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Fourier transform infrared spectrometry (FT–IR) showed that strong interactions existed between oM and EP/PU matrix, and oM had some effect on hydrogen bonding of these EP/PU IPNs nanocomposites. Positron annihilation spectroscopy (PALS) and differential scanning calorimetry (DSC) measurements were used to investigate the effect of oM and PU contents on free volume and glass transition temperature (T_g) of these nanocomposites. The PALS and DSC results clearly showed that the presence of oM led to a decrease in the total fractional free volume, which was consistent with increasing T_g upon addition of oM, ascribed to increasing hydrogen bonding in interfacial regions of oM and EP/PU matrix and enhancing the miscibility between EP phase and PU phase. In addition, with increasing PU content, the total fractional free volume increased, corresponding to decreasing T_g.

Keywords: Interpenetrating polymer networks; Nanocomposites; Free volume; Glass transition temperature

1. Introduction

Polymer/layered silicate nanocomposites show dramatic improvement in mechanical properties, barrier properties, thermal resistance and flame retardant properties at lower clay loading in contrast to traditional polymer composites, which has attracted much attention in many fields [1–8]. It is

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a well-established fact that the dispersion and exfoliated degree of layered silicate in polymer matrix are responsible for improving properties of polymer/layered silicate nanocomposites. This has motivated many researchers in both industry and academia to develop new methods to improve the dispersion and exfoliated degree, characterized by TEM, XRD, etc, of layered silicate. Recently, Yaron et al. [9] investigated the microstructure of organic montmorillonite in atomic dimensions with high resolution electron microscopy. The dispersed microstructure of the clays in the nanocomposites was also characterized by small-angle neutron scattering (SANS), ultra-small-angle neutron scattering (USANS), small-angle X-ray scattering (SAXS) [10]. However, reports about effects of layered silicate on microstructure of polymer matrix are limited [11,12].

Free volume, 'micro-holes' existing in polymers, has an effect on the physico-mechanical behavior and performance of polymers. Positron annihilation lifetime spectroscopy (PALS) technique is an effective method to detect the free volume, and has been widely used in studying polymer systems at molecular level in the recent years. This technique utilizes the interactions between the positrons and the electrons from the host material. Although there are a number of papers concerning PLAS applications in the study of microstructure of polymers and polymeric blends [13–15], attention has seldom been focused on the effect of layered silicate on microstructure of nanocomposites [16,17]. To the best of our knowledge, the free volume of interpenetrating polymer networks nanocomposites containing layered silicate has not been investigated using PALS technique. Moreover, the free volume is closely related with the hydrogen bonding of IPNs, and it is the space available for segmental motions, such as the large scale motions associated with the glass transition [18]. Owing to reflecting microstructure of polymer blends and compatible ability of components, the glass transition temperature (T_g) of IPNs was investigated widely [19–21].

Therefore, the objective of the work is to investigate effects of organophilic montmorillonite (oM) on the free volume, hydrogen bonding and T_g of the EP/PU IPNs nanocomposites by PALS technique, FT–IR, DSC, as based on our earlier study [22–24]. The results obtained in this work will be helpful for understanding the relationship between microstructure and physical properties of the EP/PU IPNs nanocomposites containing oM.

2. Experimental

2.1. Materials

The commercial 2,4-toluene diisocyanate (TDI) and Octadecylammonium chloride were made in Shanghai Chemical Reagent Co. (China). Commercial castor oil, diglycidyl ether of biphenol A (DGEBA) and 2,4,6-tri (dimethylaminomethyl) phenol (DMP-30) were made in Tianjin Chemical Co. (China). The sodium montmorillonite with a cation exchange capacity (CEC) of 90–100 mmol/100 g was provided by South Clay Co. (China). The method for preparing organic montmorillonite was similar to that of Chang et al. [25]. Castor oil and DGEBA were dried under a vacuum prior to use.

2.2. Synthesis of EP/PU IPNs and EP/PU IPNs nanocomposites

A typical synthesis process is similar to our previous study. A weighed amount of castor oil was placed in a round-bottomed flask, heated until 60 °C, and thoroughly mixed with a predetermined amount of TDI (NCO/OH ratio is 3:5), the reaction system was stirred vigorously with a Teflon-coated magnetic stir bar, under a dry nitrogen atmosphere, for about 45 min to form a urethane prepolymer. Then a predetermined amount of the epoxy precursor (DGEBA, EP/PU = 75:25) was added to the system which was stirred for a while before adding 1.5%, by weight, of DMP-30 (based on the amount of DGEBA). The mixture was degassed under a vacuum for several minutes, then poured and pressed into the preheated Teflon molds. The filled molds were heated until 120 °C and were cured at that temperature for several hours, then the EP/PU IPNs were synthesized, marked as EP/PU0.

The epoxy precursor and different amounts of oM (1%, 3%, 5%, by weight, based on the amount of the epoxy precursor) were placed in a round-bottomed flask, heated until 80 °C and stirred vigorously for about 8 h, then the PU prepolymer were added into the epoxy precursors containing oM. The following steps were the same as synthesis of EP/PU IPNs. The EP/PU IPNs nanocomposites with different oM content were prepared, marked as EP/PU1, EP/PU3 and EP/PU5, respectively. In these nanocomposites, the weight ratio of EP and PU is 75:25. Changing the weight ratio of EP and PU, we prepared EP/PU nanocomposites with different PU contents.