



Study on miscibility of poly(vinyl chloride) and polyepichlorohydrin by viscometric and thermal analysis

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ABSTRACT

Viscometric analysis was carried out to study the miscibility of poly(vinyl chloride) (PVC) and polyepichlorohydrin (PECH) in various solvents, tetrahydrofuran (THF), methyl ethyl ketone (MEK) and dimethylformamide (DMF). The Krigbaum–Wall criterion is used here to evaluate the miscibility of the two components, and Δb is introduced which can be calculated from the viscosity curves. The results show that their attractive forces are predominant when dissolved in THF, while in MEK and DMF repulsive forces play a leading role. This is attributed to different solubilities of the two polymers in the three solvents and to different influences of the solvents on the conformation of the polymers. Thermal measurement was performed by differential scanning calorimetry to investigate the glass transition temperature (T_g) of the blends prepared from the three solvents. Phase separation is observed for the samples made from MEK and DMF, while for THF the sample exhibits a single phase.

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1. Introduction

Polymer blending has been of great concern in the past decades. The combining of two or more different polymers is often used to obtain desirable features [1]. However, their performance depends on the miscibility of the blend components. Therefore, miscibility determination of polymer blends is of considerable importance. Many experimental and theoretical methods have been used to investigate polymer miscibility, such as dynamic mechanical and thermal methods, electron microscopy, etc., which are costly and sophisticated. In contrast, dilute solution viscometry (DSV) is simple and inexpensive, and could also reveal important information regarding the polymer–polymer miscibility. Therefore, it is broadly employed in miscibility investigation [2–9].

For the ternary system of polymer A–polymer B–solvent, the principle of using a dilute solution viscometry to measure the miscibility is based on the assumption that the molecules of component polymers may exist in a molecularly dispersed state and undergo a mutual attraction or repulsion which will influence the viscosity of the system. The repulsive interactions cause shrinkage of macromolecular coils so that the viscosity of the ternary solution is less than that of the corresponding binary solution. On the contrary, if the interactions between two polymers are attractive, the coils tend to spread and the average volume of each molecule becomes larger which leads to an increase of the viscosity. To date, a number of criteria to evaluate the miscibility between polymers have been proposed [10–13]. As published by Krigbaum and Wall [14], the Δb parameter, calculated using the equation: $\Delta b = b_{12} - b_{12}^*$, can be utilized to evaluate the presence of interactions. If $\Delta b > 0$, attractive forces are dominant which proves the miscibility. If $\Delta b < 0$, repulsive forces prevail and immiscibility is expected. In the equation above, b_{12} and b_{12}^* are both calculated from

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viscometric parameters which correspond to experimental and theoretical miscibility parameters, respectively.

In a ternary (polymer A–polymer B–solvent) system, thermodynamic interactions play the most important role, including not only the interactions between the same polymers and between different polymers, but also the interactions between each polymer and the solvent. Different solvents may influence miscibility between polymers and the viscosity of the system in different ways. As is well-known, in polymer–solvent binary systems, the interaction between polymer and solvent molecules to a large extent depends on the solvent selected. For instance, if the polymers are dissolved in a solvent below temperature θ , the attractive interaction may dominate. If the polymers are dissolved in a solvent above temperature θ , the repulsive interaction should be expected. The effect of solvent on the miscibility of polymers has been reported before [4,15], but still not enough attention has been attracted.

Our present study focuses on the miscibility of polyvinylchloride (PVC) and polyepichlorohydrin (PECH) in different solvents, tetrahydrofuran (THF), methyl ethyl ketone (MEK) and dimethylformamide (DMF), respectively. PECH is an important amorphous elastomer and is used in various branches of technology [16,17]. Though the viscometric method is commonly used and interactions between many polymer pairs have been investigated, the miscibility of PVC/PECH has not been studied before. The miscibility was examined under two different conditions: (1) in dilute solution, using viscometry determination and (2) in cast films, using differential scanning calorimetry (DSC). It was shown that PVC and PECH are well miscible in THF, as the deviation in reduced viscosity of the experimental results of the blend from the theoretical one is positive. However, in DMF and MEK, the polymer pair does not have good miscibility. The miscibility parameter, Δb , also shows the same phenomenon, using the Krigbaum–Wall criterion [14]. DSC characterization is another way to investigate miscibility and more direct to comprehend. Similar results were obtained.

2. Experimental

2.1. Materials

PVC (SG-5, $M_w = 136,014$ g/mol, $M_n = 80,464$ g/mol, PDI = 1.69) used in this study is a commercial product of Jilin Petrochemical Company. PECH was purchased from Sigma–Aldrich Co. with the molecular weight of 700,000 g/mol. THF, DMF and MEK were all bought from Tiantai Chemical Reagent Factory (Tianjin, China).

2.2. Dilute solution viscometry (DSV)

A dilution type Ubbelohde viscometer was used. All the viscosity measurements were performed at 30 °C. The two polymers were weighed with different compositions and dissolved in the three solvents, respectively. The concentration of all the solutions was kept at 1.2 g/dl and the ratios of PVC/PECH in the mixture were 100/0, 90/10, 70/

30, 50/50, 30/70, 10/90 and 0/100. Viscosity was measured and some important values to determine the miscibility were obtained. In the preparation step, continuous stirring was performed for 24 h to guarantee that all the solid samples dissolved. The flow time of the solvent was measured first. Afterwards the stock solution with known weight was added to the viscometer. A certain amount of solvent was added to the solution successively to get a concentration gradient. The intrinsic viscosity, $[\eta]$, was obtained from the Huggins equation [18]:

$$\eta_{sp}/C = [\eta] + bC \quad (1)$$

where η_{sp} is specific viscosity and $b = k[\eta]^2$ where k is the Huggins constant.

2.3. Preparation of the blending films

The two polymers were weighed with different compositions and dissolved in different solvents. After that, 24 h stirring was performed to make it uniform. The total weight of the polymers was 2 g and 60 ml of each solvent was used. When the solid samples were all dissolved, the solutions were poured into Petri dishes with a diameter of 60 mm. The total weight of polymer blends and Petri dish was obtained prior to preparing the solution. A horizontal plane was used to make films with even thickness. The films were kept under ambient conditions for 4 d and moved into a vacuum oven at 50 °C for another 2 d to get rid of the residual solvent. After cooling to room temperature, the samples were weighed several times to check whether residual solvent remained, until the polymer weight was equal to the previous weight.

2.4. Differential scanning calorimetry (DSC)

PVC/PECH (75/25 w/w) was characterized on a Mettler Toledo 821^e differential scanning calorimetry apparatus. Nitrogen was used as the purge gas. The program temperature was set from –40 to 100 °C, and the heating rate was 20 °C/min.

3. Results and discussions

3.1. Viscometric measurements

The plots of reduced viscosity (η_{sp}/C) versus concentration (C) for the two pure polymers and their blend solutions of PVC/PECH-70/30 in the three solvents are shown in Figs. 1–3, respectively. It is obviously seen that for all the samples of different ratios, pure PECH has the highest reduced viscosity while PVC has the lowest one. This is attributed to the better chain softness of PECH which results in better mobility and more interactions between polymers. However, PVC is more rigid and harder to change the conformation, and attractive interaction is less. According to the additivity of the reduced viscosity, there is a dashed line between the curves for PVC and PECH in each graph, respectively. It signifies the theoretical curve for PVC/PECH-70/30, which is based on the assumption that no attractive or repulsive forces lie between different

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