



Rheological behavior of poly(vinyl butyral)/polyethylene glycol binary systems

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ABSTRACT

The influences of mass fraction of poly(vinyl butyral) (PVB) and temperature on the rheological behavior of poly(vinyl butyral) (PVB)/polyethylene glycol (PEG) 200 binary system were investigated by a rotational rheometer with parallel plates. The results show that the complex viscosity and zero-shear viscosity increase with the increase of PVB mass fraction, shear thinning behavior is observed for all the PVB/PEG systems and enhanced with the increase of the PVB mass fraction. Both the elastic and loss modulus increase with the increase of PVB mass fraction. The flow recovery of the system increases with the increase of PVB mass fraction and shearing frequency. The PVB/PEG200 systems show an upper critical solution temperature (UCST) behavior, and remain homogeneous irrespective of shear force at 150 °C and 160 °C while phase separation occurs at 140 °C. The results show that the viscosity fits the Arrhenius model very well in homogeneous region, yielding an activation energy of 30.01 kJ/mol. In phase-separated region, the complex viscosity significantly deviates from the Arrhenius model.

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1. Introduction

Polyvinyl butyral (PVB) is regarded as a random copolymer of vinyl butyral and vinyl alcohol units. The vinyl alcohol unit is polar and hydrophilic and the vinyl butyral unit is hydrophobic. As an innocuous and tasteless polymeric material, PVB can endure low temperature, light, change in humidity, bacteria, microorganism, alkali and diluent acid [1]. Moreover, it reveals some hydrophilicity because of its hydroxyl groups. Therefore, PVB seems to be an attractive material for preparing the membrane [1–3].

Thermally induced phase separation (TIPS) process is one of the alternative valuable methods to prepare microporous membranes, which can be applied to a wide range of polymers, especially those that cannot be formed into membranes due to the poor solubility [4–7]. In the TIPS process, polymer and diluent are firstly mixed at an elevated temperature to form a homogeneous solution, and then extruded from the spinneret into a coagulation bath to induce phase separation and solidification [8,9].

PVB microporous membranes have been prepared via TIPS with polyethylene glycol (PEG) 200 as diluent [10,11]. In the spinning process both phase separation and rheological behavior have an influence on the shape and morphology of the hollow fiber membranes [11,12]. Rheology not only determines the stresses and flow stabilities, but also controls the microstructure and mechanical properties of the products. Therefore, the rheological study on the behavior of PVB/PEG200 system helps to understand the structure and properties

of the PVB hollow fiber membranes. This is due to the fact that flow is widely involved in processing such as extrusion, fiber spinning, and injection molding to fabricate polymeric materials into useful objects. In the fabrication of hollow fiber membranes via TIPS, the properties of hollow fiber membranes are known to be affected by flow conditions during extrusion due to molecular orientation. From the rheological perspective, the intensity regions in fiber formation are the shear flow during extrusion through the spinneret and elongational flow in the air gap region prior to immersion into the coagulation bath. Both of these types of flow lead to molecular orientation in the fiber structure [13–16]. The obtained rheological results elucidate that weak molecular interactions are dominant in the process of extrusion of polymer solution, the complex viscosity tends to increase with the increase of PVB concentration, resulting it gets difficult for the coagulant to penetrate the polymer matrix after the nascent hollow fiber membrane enter coagulation bath. Thus, the formation of macrovoids is suppressed and the permeate flux of the hollow fiber membrane decreases [11–17].

The spinning of hollow fiber membranes is a very complex process, rheological properties under shear and elongation further have effect on chain conformation, i.e. orientation in the skin layer. Therefore, detailed rheological studies are important to the behavior of PVB/PEG200 system extruded from the spinneret and the final properties of the PVB hollow fiber membranes via TIPS. However, there are so far no reports on the rheological properties of the PVB/PEG200 system. In this work, we focus on studying the effect of temperature and mass fraction of PVB on the rheological properties of the polymer–diluent system. The rheological properties were obtained from oscillatory shear measurements examining the shear viscosity, storage and loss modulus, melt miscibility and flow recovery characteristics.

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2. Experimental

2.1. Materials

Poly(vinyl butyral) (PVB), vinyl butyral part is 45%–49%, was purchased from Sinopharm Chemical Reagent Co., China. Polyethylene glycol (PEG, $M_w = 200$) used as diluent was supplied from Sinopharm Chemical Reagent Co., China. All the chemicals were used without further purification.

2.2. Preparation of PVB/PEG200 binary system

PVB/PEG200 samples were prepared by melt mixing on the Haake Rheocord 90 with Rheomix 600 mixer at 160 °C and 40 rpm. The mixing continued until a constant torque was reached. The mass fraction of PVB is indicated in Table 1, and the samples were denoted as PVB20, PVB25, PVB30 and PVB35. The samples for rheological testing were prepared by compression molding at 160 °C for about an hour in the form of 40 mm diameter disks with 1.5 mm in thickness. To avoid water absorption, the samples obtained were stored in a vacuum oven at 80 °C for two days before use.

2.3. Rheological testing

The rheological behaviors of the binary systems were measured with a rotational rheometer (AR2000, TA instruments) using parallel plates with a diameter of 40 mm and a gap of 1.0 mm. The specimen was melted at 160 °C between the parallel plates and kept for 3 min at the temperature to remove the residual stress. Dynamic frequency sweeps were performed over the range of 0.05–600 rad/s at 120, 140, 150 and 160 °C, using strain values determined with a dynamic strain sweep to lie within the linear viscoelastic region. To avoid any oxidative degradation of the samples, all measurements were conducted under nitrogen atmosphere.

3. Results and discussion

3.1. Effect of mass fraction of PVB

Rheological behavior is very critical to understand processability and structure–property relationships of polymers. In rheological tests, small-amplitude oscillatory shear was conducted within the linear visco-elastic region of the sample. The internal structure of the sample would not be ruptured during the test. The sample was just probed rheologically for its “unperturbed structure”. When a macromolecular chain is subjected to a small shear deformation, the chain deforms from the initial spherical shape to an ellipsoid. When the shear is removed, the deformed chain relaxes and recovers its initial equilibrium spherical shape. Polymer melts respond to small-amplitude oscillatory shear through this deformation–relaxation process. First dynamic strain sweep test was applied to samples in order to characterize strain dependence of the viscoelastic properties of the samples and to determine linear viscoelastic region. Since the shear storage modulus (G') is a more sensitive rheological function than the loss modulus (G'') to the structural changes of the polymer, only the storage modulus curves are presented here. Dependence of storage modulus on the strain for the PVB20 sample is shown in Fig. 1.

Table 1
PVB/PEG200 binary system compositions.

Sample codes	PVB (mass fraction)	PEG200 (mass fraction)
PVB20	20%	80%
PVB25	25%	75%
PVB30	30%	70%
PVB35	35%	65%

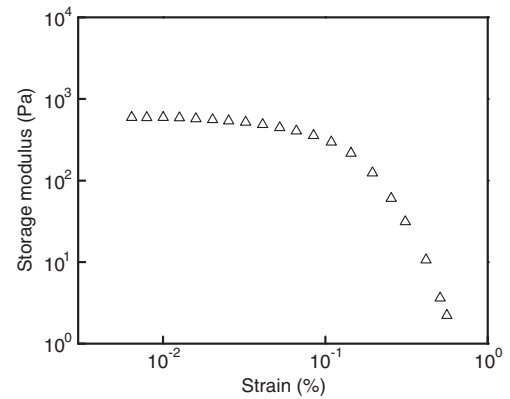


Fig. 1. Storage modulus versus strain (%) curve.

Since the structure of polymer might be destroyed by high shear amplitude, it is necessary to use very low amplitude [18]. Strain sweep tests show that the sample is in the linear viscoelastic region when the strain is below 10%. Within this region, 2.5% strain was chosen as the strain for all small-amplitude oscillatory frequency sweep tests.

Dynamic frequency sweep tests were conducted in linear viscoelastic region to further study the rheological characteristics of the PVB/PEG200 system. From these experiments, insights were gained into the processing characteristics of these samples. Of interest, was the frequency dependence of the storage and loss moduli as related to the shear viscosity and shear rate dependence. Other melt characteristics include zero-shear viscosity, melt elasticity and melt miscibility.

Fig. 2 shows the angular frequency (ω) dependence of the complex viscosity η^* at 160 °C. It illustrates that the complex viscosity decreases with increasing of frequency for all the samples. This is due to the strong shear thinning behavior of the polymers. Entanglements between branches and chain segments may occur randomly, modifying the entanglement density of these polymers under shear flow. Consequently, a nonlinear rheological behavior is observed. It is also seen that complex viscosity of the samples increases with the increase of PVB mass fraction.

Cross model [19] was applied to fit the relaxation spectra, it can be expressed as Eq. (1):

$$\eta^* = \eta_0 / [1 + (\tau\omega)^m] \quad (1)$$

Where ω is the oscillation angular frequency, η_0 is the zero shear viscosity, τ is a characteristic relaxation time, and m is a dimensionless exponent that is independent of temperature. The zero shear viscosities obtained from cross fitting are listed in Table 2. The rate at which shear thinning occurs for a polymer is of great importance during polymer processing. To compare the shear thinning behavior of

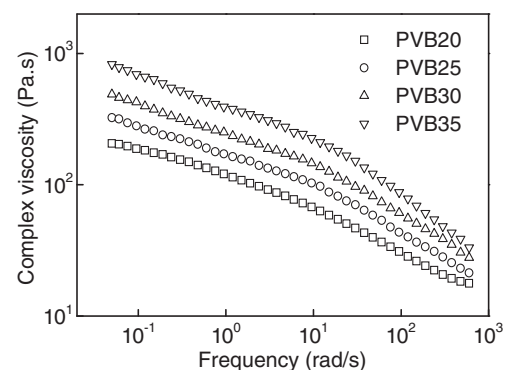


Fig. 2. Complex viscosity η^* versus frequency for different samples at 160 °C.

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