Study on extensional viscosity of acrylic adhesive

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ABSTRACT

In this paper, transient extensional viscosities of acrylic adhesives were studied using Extensional Viscosity Fixture (EVF) in rotation rheometer at 120 °C under different extensional rates. Extensional viscosity is an important parameter to evaluate extensional behavior of adhesives. Strain hardening was observed during extension for tested adhesives. Effects of molecular weight and tackifier addition on transient extensional viscosities were also investigated. Addition of tackifier would decrease transient extensional viscosities of tested acrylic adhesives. In addition, extensional viscosities were compared to complex viscosities obtained from linear oscillation shear tests at 120 °C. Extensional viscosity is more sensitive to addition of tackifier compared to shear viscosity.

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1. Introduction

Polymer melt processing involves significant extensional deformation, like fiber spinning, extrusion and film blowing. Adhesive production and application are also affected by extensional or elongational deformation besides shear movement. Adhesive fibril formation and stretching during debonding are partially governed by extensional viscosities. Extensional rheology plays an important role in tack and peel experiment for adhesives [1–3].

In 1970s and 1980s, Vinogradov et al. [4–9] started to study uniaxial extensional rheology of various polymers at different state, from fluid to high-elastic and glassy states. The effects of molecular parameters [4,5,7] and normal alcohol liquid media [7,8] were studied on deformation and rupture of non-cross-linked linear polymers. The liquid media used were ethanol, propanol, butanol, amyl alcohol, isopropyl alcohol and water. They established unexpectedly simple relations connecting the parameters that characterize the rheological properties of polymers at deformation rates and stresses tending to zero with their ultimate strength and long term durability [9]. For a polymer melt or a polymer solution, it is difficult to get pure extensional movement with large deformation. The variation of extension viscosity is more complex than that of shear viscosity. There are three types of variation trends of melt extensional viscosities for different polymers: extensional thinning like High Density Polyethylene (HDPE), keeping constant like Polystyrene (PS), and extensional hardening like Low Density Polyethylene (LDPE) [10]. Various fixtures have been developed for the measurement of extensional viscosity. Arabo et al. measured extensional viscosities of

hard wheat flour dough using capillary rheometer [11]. Zatloukal et al. developed a novel orifice die with entrance pressure drop techniques, which allows more precise extensional viscosity measurement compared to conventional orifice dies [12]. Two dual wind-up extensional fixtures are also commercially available like Sentmanat extensional rheometer from Xpansion Instruments [13,14] and the Extensional Viscosity Fixture (EVF) from TA instruments [17]. Bach used filament stretching rheometer to measure the extensional viscosity of polymer melts at high temperatures [18]. Yang et al. [19] used a melt-spinning technique for melt-strength and extensional viscosity of low-density polyethylene and poly(butylenes succinate) blends. Extensional viscosity is widely used in polymer branching study, especially for LDPE [20–22] and fluorothermoplastics [17]. Different models have been proposed for calculation of extensional viscosities. Trouton proposed a simple relationship that the viscosity under tension was three times of that under simple shear [23]. Barnes et al. predicted simultaneously both shear and extensional viscosity using a simple equation

$$\eta_s(\text{II}_D) = \eta_0 / \left[1 + (K_1 \text{II}_D)^n \right] \text{ and } \lambda(\text{II}_D) = \lambda_0(\text{II}_D) = \lambda_0 / [1 + K_2 \text{II}_D], \quad (1)$$

which gives a reasonable estimate of the steady-state elastic properties [24]. Here, II_D is the second invariant of the deformation tensor. $\lambda(\text{II}_D)$ and $\eta_s(\text{II}_D)$ are the deformation rate-dependent relaxation time and viscosity, respectively. K_1 and K_2 are parameters with dimensions of time, n is a numerical constant. Liang et al. proposed a new modified cross model equation

$$\eta_E = \left(\eta_0 / \left(1 + (\lambda \dot{\varepsilon})^{1-m} \right) \right) \left(3 + k \dot{\varepsilon} / (\lambda_1 + \dot{\varepsilon}) \right) \quad (2)$$

to describe the relationship between melt extension viscosity and extension strain rate during single shaft elongation flow of polymeric materials within a wide range of extension strain rates [10].

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Here, η_0 is zero shear viscosity, $\dot{\varepsilon}$ is extension strain rate, λ is relaxation time, λ_1 is the relaxation time reflected at the beginning position of extension hardening, k presents the extension hardening property. Cogswell model [11,25,26] can be used for uniaxial extensional viscosity measurement as follows

$$\eta_E = \sigma_E / \dot{\varepsilon}_E = (9(n+1)^2 P_o^2)/(32\tau_{co}\dot{\gamma}_{ap}) \qquad (3)$$

Here, $\dot{\gamma}_{ap}$ is apparent shear rate, τ_{co} is corrected wall shear stress, P_o is capillary entrance pressure drop, n is the flow behavior index. Molecular stress function (MSF) theory suggests that tube stretching is a function of deformation history rather than deformation rate [22,27]. It was revealed that by using Zatloukal's novel orifice die design corrected Cogswell model is more precise in uniaxial extensional viscosity prediction than Binding [28] and Gibson models for highly branched and slightly branched polymer melts [12]. For linear polymer melts, Binding and Gibson models were found to provide excellent capability to predict extensional viscosity data from entrance pressure drop measurement [12].

Adhesive researchers have done lots of work on extensional rheology by probe tack or tensile test. Creton et al. did lots of work on both linear and nonlinear rheological properties of acrylic adhesive using tensile-test and probe tests [3,29–32]. The tensile curves of lightly crosslinked acrylic networks show a very pronounced softening at intermediate strains followed by a pronounced hardening at large strains [29,30]. There is little work that has been reported on direct measurement of extensional viscosity of adhesives, partially due to the measuring difficulties. Christensen et al. measured transient extensional viscosities of a polyisobutylene-based pressure-sensitive adhesive (PSA) in a filament stretching instrument at three stretch rates [1]. The data agree well with linear viscoelasticity at low strains which deviate from linear viscoelasticity due to strain hardening of the adhesives. Only non-linear equation incorporating the bounded strain-hardening nature of the PSA offers nearly quantitative prediction of peeling force [1].

In this paper, we used Extensional Viscosity Fixture (EVF) in ARES-G2 rotation rheometer from TA Instruments to evaluate transient extensional viscosity of acrylic adhesives with and without rosin tackifier.

2. Materials and experiments

All samples are common acrylic adhesives made in 3M China lab. Two samples with different Mw, S (Mw above 1,000,000, Polydispersity PD $\approx$ 8.2) and S1 (Mw $\approx$ 500,000, PD $\approx$ 5.2), were used to evaluate the effect of molecular weight. Sample S with 21.6 wt% (27.5 g tackifier/100 g polymer) and 27.3 wt% (37.5 g tackifier/100 g polymer) rosin tackifier were used to investigate the effect of tackifier. T_g of rosin and adhesive polymer are about 45 °C and −58 °C, respectively, measured by DSC (Discover DSC, TA Instruments, US) with 10 °C/min heating rate. These two samples were labeled as S+21.6tack and S+27.3tack, respectively. All samples were thermomolded into rectangular shape (8 mm × 10 mm × 0.7 mm) at 100 °C and 0.6 MPa for 3 min.

Extensional viscosities were measured at 120 °C with Extensional Viscosity Fixture (EVF) in rotation rheometer (ARES-G2, TA instruments, US). EVF contains two cylinders, which are used to wind up sample. One cylinder is rotating, the other measures the force. In order to wind up the sample equally on both sides, the rotating cylinder moves on a circular orbit around the force measuring cylinder while rotating around its own axis at the same time [15]. Schematic of EVF can be found in Ref. [15]. Fig. 1 is the picture of EVF in our lab.
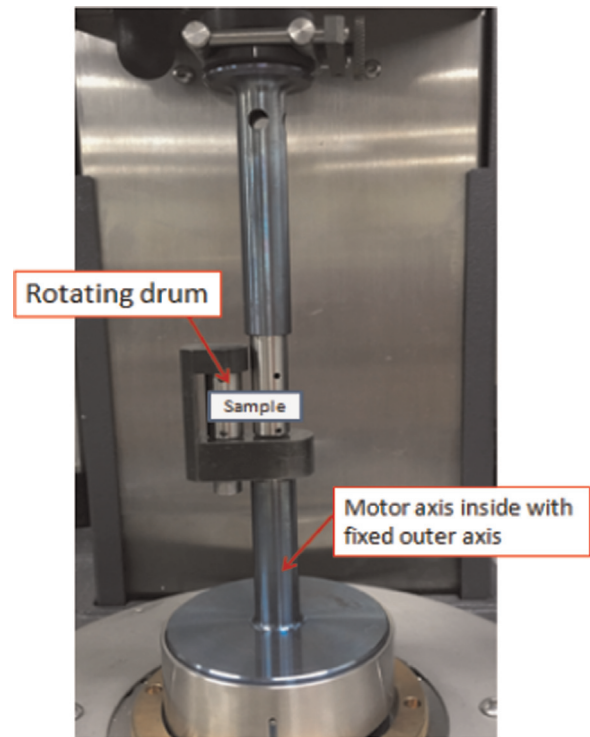

Fig. 1. Picture of Extensional Viscosity Fixture (EVF).

Transient extensional viscosity is defined as

$$\eta_E(t) = \sigma_E(t)/\dot{\gamma}_E \qquad (4)$$

Here, $\sigma_E(t)$ is extension stress and $\dot{\gamma}_E$ is extension rate. Various extension rates of 0.02 s^{-1}, 0.05 s^{-1}, 0.1 s^{-1}, 0.2 s^{-1} and 0.5 s^{-1} were applied until reaching the Hencky strain of 3.5. The Hencky strain is used for large deformations, and is defined as ln (L_t/L_o). Here, L_o is initial length and L_t is real time length.

Complex shear viscosity measurement was conducted using the same rotational rheometer (ARES-G2, TA Instruments, US) with parallel plate 25 mm geometry. Oscillatory frequency sweep was conducted under controlled strain of 5% at 120 °C in linear viscoelastic region.

3. Results and discussions

Fig. 2 shows transient extensional viscosity $\eta_E(t)$ as a function of Hencky strain for sample S with extensional rates of 0.01 s^{-1}, 0.05 s^{-1} and 0.1 s^{-1}. Samples undergo rupture at 0.05 s^{-1} and 0.1 s^{-1} before reaching Hencky strain of 3.5. $\eta_E(t)$ increases from about 10^4 Pa s to 10^7 Pa s as Hencky strain increases. There is about three to four decade increase in $\eta_E(t)$ during elongation. Higher extensional rate leads to lower $\eta_E(t)$, which is similar to shear viscosity. As shown in Fig. 2, the crossover of two tangent lines denotes start of strain-hardening, at which the extensional viscosity steeply rises. Strain hardening is commonly observed in elongational flow of polymer melts [38–42], However, there is still debate on the mechanism of strain hardening. Minegishi et al. reported that molecular entanglement affects the intensity of the strain hardening [33]. Addition of ultra-high molecular weight component would intensify straining hardening, and strain hardening of homogeneous polymers is closely related to the long-time relaxation caused by the existence of the long-chain branching or a small amount of UHMW chains [33]. Wager et al. suggested that the origin of strain hardening is chain stretching caused by a reduction of the tube diameter with increasing deformation [34]. Presence of long-chain branches would