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Study on Evolution of Apparent Viscosity in Poly(lactic acid)-Based Polyurethanes

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Abstract. The apparent viscosity of polylactic acid-based polyurethane (PLA-TPU) is influenced by the reaction progress, temperature, and shear rate. PLA-TPU with varying degrees of reaction was synthesized using diphenylmethane diisocyanate, polylactic acid glycol, and 1,4-butanediol as raw materials. The chemical structure, rheological kinetics, and viscosity model of the product were investigated using Fourier transform infrared spectrometer, gel permeation chromatography, and a rotary rheometer. The results indicated that the urethanization reaction followed second-order reaction kinetics, with an activation energy of 31.84 kJ/mol. At a shear rate of 1 s-1, the reaction system was proportional to the weight average molecular weight to the power of 2.88. Temperature variations followed the Arrhenius equation, and the viscous flow activation energy was 12.83 kJ/mol. Its apparent viscosity's shear thinning behavior could be described using a power law model, with a flow index of 0.5694. This model enables rapid prediction of the apparent viscosity of the PLA-TPU reaction system under given conditions, and the modeling process also serves as a reference for other stepwise polymerization synthesis studies.

Keywords: PLA-TPU; Rheokinetics; Apparent viscosity; Power-law model.

1. Introduction

Polylactic acid-based polyurethane (PLA-TPU), as a thermoplastic polyurethane, exhibits excellent biocompatibility, mechanical strength, and ease of processing, making it widely used in biomedical applications[1-3]. PLA-TPU typically undergoes one-step bulk polymerization, where the apparent viscosity of the system is influenced by factors such as reaction time，temperature, and shear rate[4,5]. To enhance the design of polymerization reactors, it is imperative to establish a rheological kinetic equation correlating system viscosity with the reaction progress[6]. Simultaneously, a constitutive equation should be formulated to describe the relationship between system viscosity and shear rate during stirring. For the linear stepwise polymerization reaction of PLA-TPU, a more effective approach to correlate the gradual polymerization process is to utilize molecular weight as a pivotal parameter. By employing linear growth theory to regress kinetic parameters, and utilizing Flory's empirical equation and the non-Newtonian model, we can characterize the dependence of system viscosity on molecular weight and shear rate[7,8].

In this experiment, diphenylmethane diisocyanate, polylactic acid glycol, and 1,4-butanediol were utilized as raw materials to prepare PLA-TPU polymerization systems with varying degrees of reaction at temperatures ranging from 80 to 160 ℃. We employed GPC and steady-state rotational rheological analysis to establish the rheological kinetics and constitutive equation models for PLA-TPU bulk polymerization.

2. Eexperimental

2.1 Materials

Polylactic acid glycol (PLA-OHs, Mn=1000), Guanghua Weiye Co., Ltd. 4,4 '- diphenylmethane diisocyanate (4,4'-MDI), Wanhua Chemical Group Co., Ltd. 1,4-Butanediol (1,4-BDO), Di-n-butylamine (DBA), China National Pharmaceutical Group Chemical Reagent Co., Ltd.

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2.2 Preparation

Set the temperature of the oil bath according to the reaction, weigh 4,4 'MDI, PLA-OHs, and 1,4-BDO in a mole ratio of 2:1:1, melt and remove water at 100 ℃, mix PLA-OHs and BDO in a three necked flask under nitrogen protection, add 4,4' MDI, and start recording the reaction time. After a certain reaction time, add an appropriate amount of DBA to terminate the polymerization. Pour the product into the mold to solidify and conduct testing.

2.3 Measurement and Characterization

Use the spectrometer (Nicolet IS10, Thermo Fisher Scientific Co., America) to perform infrared qualitative testing on PLA-TPU samples after slicing and vacuum dehydration, using ATR mode with a testing beam range of 500~4000 cm-1 and a scanning frequency of 32 times/s.

Use the gel chromatograph (Shimadzu- LC20/ RID-20, Shimadzu Co., Germany) to determine the weight average molecular weight (Mw) of PLA-TPU samples with different reaction times, with tetrahydrofuran (THF) as the mobile phase and polystyrene (PS) as the calibration substance.

Perform rheological tests on PLA-TPU samples with different molecular weights using the rotational rheometer (Kinexus Prime Ultra+, Netzsch Co., Germany). Each sample undergoes temperature scanning and frequency scanning separately.

3. Results and Discussion

3.1 Analysis of the Chemical Structure of PLA-TPU

The FTIR spectra of PLA-TPU samples after reacting for 100 s at various reaction temperatures are presented by Figure 1. From the figure, it is observable that stretching and bending vibration peaks of the imino (N-H) appear at 3360 cm-1 and 1520 cm-1, respectively, while a stretching vibration peak of the carbonyl emerges at 1728 cm-1. These three absorption peaks collectively indicate the formation of urethane groups. The absorption peak near 3500 cm-1 corresponds to the unreacted hydroxyl (OH) in the polymerization system following the addition of the terminating agent. Notably, there is no absorption peak of isocyanate (NCO) around 2270 cm-1, suggesting that the isocyanate of MDI in the polymerization system have fully reacted with the hydroxyl in the diol and the amine groups in the terminating agent[9]. Consequently, the polymerization degree of the samples remain unchanged in subsequent tests.

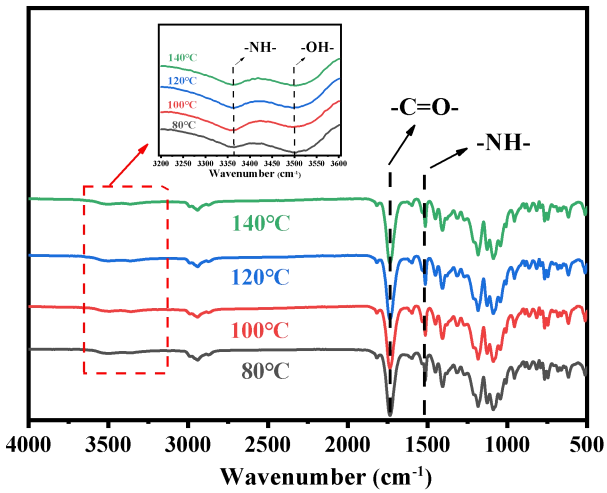

Figure 1. FTIR spectra of PLA-TPU samples.

3.2 The Variation law of Mw During PLA-TPU Polymerization Process

The reaction between isocyanates and alcohols follows second-order reaction kinetics characteristics and is based on the assumption of equal activity of functional groups and equal

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activity of diols[10]. Therefore, under the condition of feeding substances with equal amounts of reactive groups, the calculation formula for the change of Mw with reaction time during the gradual polymerization process is: [11,12]

$$M_w = (2kc_0t + 1)M_0 \quad (1)$$

$$k = A \cdot e^{\frac{-Ea}{RT}} \quad (2)$$

Where k is reaction rate constant,L/(mol·min); C0 is initial concentration of isocyanate groups,mol/L; t is reaction time,s; M0 is relative molecular weight of repeating units,g/mol; A is frequency factor; Ea is activation energy of reaction, J/mol; R is universal gas constant, 8.314 J (mol/K); T is thermodynamic temperature, K.

The variation of the Mw of PLA-TPU at different reaction temperatures over a certain reaction time is shown in Figure 2. Within the reaction time of 0.6 to 3 min, the Mw at different polymerization temperatures showed the expected linear growth trend, which is consistent with the polymerization addition mechanism of TPU polymerization system. Simultaneously observing the slope of the straight line, it can be found that the polymerization temperature not only affects the reaction rate, but also has a significant impact on the molecular weight of the product.

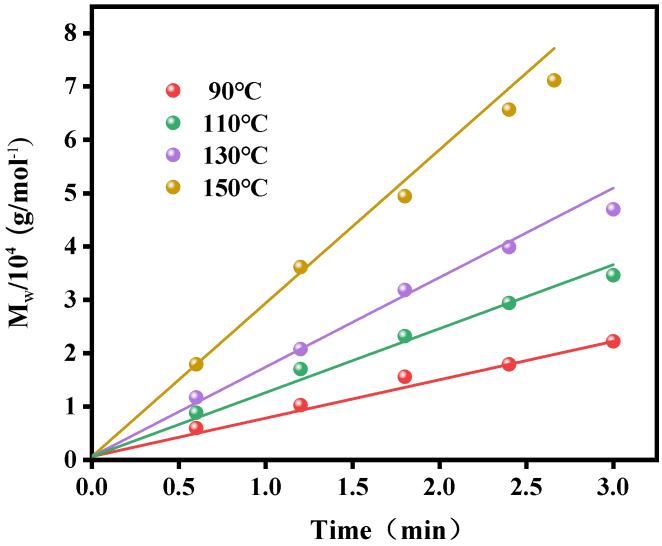

Figure 2. Variation of MW with reaction time at different reaction temperatures.

By linearly fitting equation (1), the rate constant k at each temperature can be obtained. Logarithmically fit equation (2) and obtain the reaction rate pre exponential factor A=31.4 and reaction activation energy Ea=31.84 kJ/mol through regression analysis. By substituting the kinetic parameters into equations (1) and (2), the variation of Mw of PLA-TPU with reaction temperature and time can be obtained.

$$M_W = 2.397\times10^8 te^{\left(\frac{-31.84\times10^3}{RT}\right)} + 652 \quad (3)$$

3.3 Rheological Kinetics of PLA-TPU Polymerization System

According to the free volume theory, when the testing temperature is much higher than the glass transition temperature of PLA-TPU, due to the large internal free volume, the rate of molecular displacement depends only on the ability of chain segment transition and is independent of the length of the molecule. Therefore, the Arrhenius equation can be used to describe the rate of viscosity change. Taking the reference temperature T=T0, the viscosity of the system can be expressed as: [13]

$$\eta = \eta(T_0)e^{\left[\frac{E_\eta}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]} \quad (4)$$

Where Eη is viscous flow activation energy, kJ/mol; $\eta(T_0)$ is viscosity at reference temperature, Pa·s. At low shear rates, the dependency of viscosity on Mw is represented as:

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$$\eta(T_0) = C{M_W}^N \quad (5)$$

Where C is material coefficient; N is power exponent, it is related to the critical entanglement molecular weight Mc (about 7000) of TPU. When Mw≤Mc, N is about 1-1.6, and when Mw>Mc, N is about 2.5-5

Using a rotational rheometer to characterize the changes in apparent viscosity of the PLA-TPU reaction system at 120-150 ℃. The shear rate of steady-state temperature scanning is fixed at 1s-1, and Figure 3 shows the variation of apparent viscosity of PLA-TPU with different Mw with temperature. It can be seen that the viscosity of PLA-TPU increases with the increase of Mw, and decreases nearly linearly with the increase of temperature. Select 150 ℃ as the reference temperature, substitute the viscosity measured at this temperature into equation (5), take the logarithm on both sides, and perform linear fitting to obtain the material coefficient C=2.774×10-11, N=2.8766. Take the natural logarithm on both sides of equation (4), and regress to obtain the viscosity and viscous flow activation energy of each molecular weight PLA-TPU.

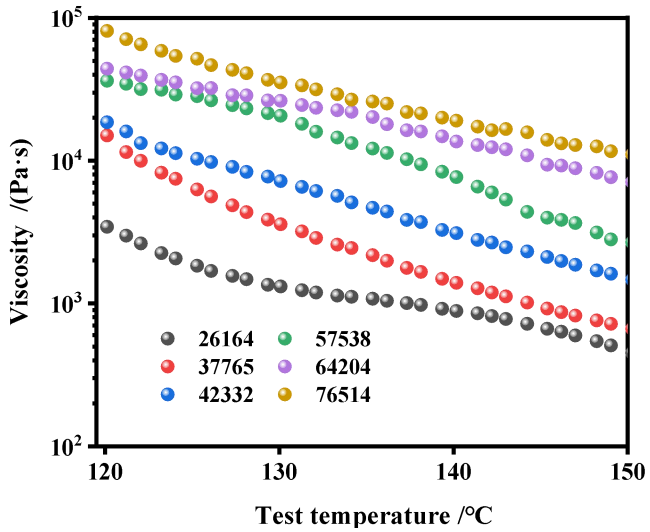

Figure 3. Changes in apparent viscosity of PLA-TPU with varying molecular weights as a function of temperature.

By substituting the average activation energy of viscous flow ($\overline{E_\eta}$=12.83 kJ/mol) into equations (4) and (5), the relationship between viscosity, Mw, and temperature in the PLA-TPU polymerization reaction system under shear rates of 1s-1,120-150℃ can be obtained. The temperature in equation (6) is the rheological test temperature, which is independent of the reaction temperature. By combining equations (3) and (6) and making the temperatures equal in both equations, the rheological kinetics of the PLA-TPU system viscosity with reaction time and reaction temperature during the reaction process can be obtained.

$$\eta(T, M_W) = 2.774 \times 10^{-11} {M_W}^{2.8766} e^{\left[\frac{12.83\times10^3}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]} \quad (6)$$

3.4 The Constitutive Equation of PLA-TPU Polymerization System

TPU melt is usually a pseudoplastic fluid, and its apparent viscosity can be described by a power-law model as a function of rate.

$$\eta(\gamma) = K\gamma^{n-1} \quad (7)$$

Where γ is shear rate, s-1; n is melt flow index; K is consistence, Pa • s.

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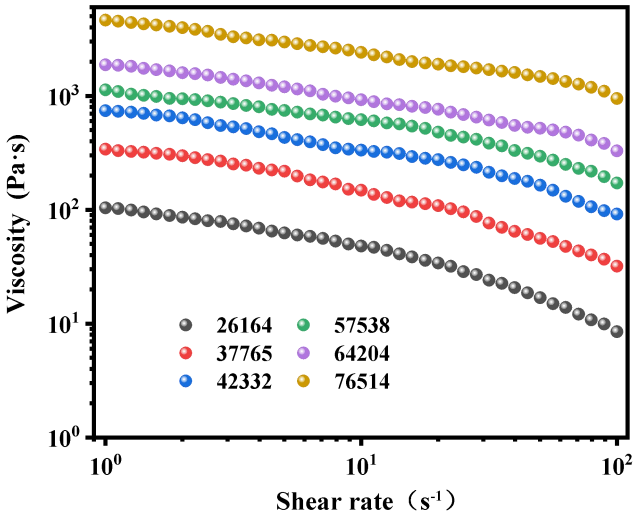

Figure 4. The variation of apparent viscosity of PLA-TPU with different molecular weights with shear rate.

Set the test temperature to 150 ℃ and perform steady-state frequency scanning on PLA-TPU samples with different molecular weights. Figure 4 shows the variation of apparent viscosity of TPU with different molecular weights with shear rate. The reaction system exhibits power-law fluid characteristics, and the viscosity of PLA-TPU decreases with increasing shear rate, and the trend of change is similar.

Take the logarithm of both sides of equation (7) and perform linear regression. Obtain viscosity coefficients of different molecular weights and flow indices at 150 ℃

According to the definition of viscosity, it is found that K in equation (7) is the viscosity in equation (6). From this, it can be concluded that there is a correlation between molecular weight 25000-80000 and shear rate 1-100s^{-1}.

$$\eta(\gamma) = \eta(T,\ M_w)\gamma^{-0.4306} \tag{8}$$

The flow index in equation (8) is obtained at 150 ℃, and the effect of temperature on viscosity is only reflected in the viscosity coefficient, with negligible impact on the flow index.

4. Summary

(1) The Mw of PLA-TPU increases linearly with time. Under the reaction temperature of 80-150 ℃, the relationship between Mw and time and temperature in the polymerization process is as follows: $M_W = 2.397\times10^8 te^{\left(\frac{-31.84\times10^3}{RT}\right)} + 652$.

(2) The variation of viscosity with Mw and temperature in the PLA-TPU reaction system can be described by the Arrhenius equation. At a shear rate of 1s-1, temperature of 80-150 ℃, and molecular weight of 25000-80000 g/mol, the rheological kinetics equation of the system is: $\eta(T, M_W) = 2.774\times10^{-11} M_W^{2.8766} e^{\left[\frac{12.83\times10^3}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]}$.

(3) The PLA-TPU reaction system exhibits significant shear thinning characteristics. At shear rates of 1-100s-1, the apparent viscosity of the system can be represented by a power-law model, namely: $\eta(\gamma) = \eta(T,\ M_w)\gamma^{-0.4306}$.

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