EDITORIAL

Study of the Rheological Behavior of Polyamide 5,6 (PA5,6)

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ABSTRACT

The rheological behavior of polymer melts and polymer solutions are of great importance in polymer processing, particularly for the analysis and design of processing operations as well as understanding the relationship between structures and properties of the final-products. The (PA5,6) objective of the present work was to investigate the rheological behavior of polyamide 5,6 to obtain information on the effect of temperature on the melt behavior of polyamide 5,6 compared to that of polyamide 6. The rheological properties of polyamide 5,6 (PA5,6) have been studied by means of a Haake rheometer. The effect of temperature on the storage modulus, loss modulus, and complex viscosity was studied. The obtained results showed that the complex viscosity, storage modulus, and loss modulus of PA5,6 and PA6 decrease with increase of the temperature. It is worth noting that the complex viscosity of PA5,6 remains almost constant showing a Newtonian behavior, on the other hand, the complex viscosity of PA6 slightly decreases with the increase of shear rate exhibits a much nearly Newtonian behavior. Similar behavior was observed for other polyamides such as polyamide 6.6 and polyamide 6.,10.

Keywords: Polyamide 5,6; Polyamide 6; Rheological behavior; Storage modulus; Loss modulus; Complex viscosity.

Introduction

Linear aliphatic polyamides commonly referred to as nylons, occupy a prominent position in the realm of polymers. Nylons are semi-crystalline polymers that usually exhibit a relatively high modulus, toughness and strength that allow widespread use of this family of polymers as fibers and engineering thermoplastics(Kohan, 1995; Welgos, 1988). These attractive properties of polyamide originate mostly from the strong hydrogen bonds, which are formed between the amide groups(Morgan, 1965).

The rheological behavior of polymer melts and polymer solutions are of great importance in polymer processing, particularly for the analysis and design of processing operations as well as understanding the relationship between structures and properties of the final-products (Bai, Goodridge, Hague, Song, & Okamoto, 2014). The rheological properties of other polyamide polymers have been extensively investigated by many authors. However, there have been no publication on the rheological properties of polyamide 5,6 so far. Parrini et al. (Parrini, Romanini,

& Righi, 1976) investigated the melt rheology of nylon 6, nylon 6,6 nylon 6,10, and nylon 11. They found that the nylons behavior is quite similar and almost Newtonian regarding the flow curves and the elastic and instability properties. Bankar et al. (Bankar, Spruiell, & White, 1977) studied the rheological properties of nylon-6 at different temperatures. Utracki et al.(Utracki, Dumoulin, & Toma, 1986) investigated the melt rheology of high density polyethylene polyamide-6 blends. They reported that a temperature dependent movement of polyamide in the capillary during the extrusion and fibrillation of the polyamide phase in the extensional field occurred at all temperatures. Zhang et al (Zhang, Liu, Zhao, Wang, & Liu, 2003) investigated the rheological properties of nylon 12,12 with Haake Rheometer. They reported that the apparent viscosity of nylon 1212 is decreased with increases in shear rate, shear stress and temperature. Wang et al. (Wang et al., 2005) studied the Steady flow and dynamic viscoelastic behavior of nylon 13,13 using parallel-plate rheometer and capillary rheometer. They found that the viscoelastic behavior of the nylon 13,13 melt depends strongly on the temperature and the applied stress. Hu et al.(Hu, Wang, & Gao, 2006) studied the rheological behavior of nylon 6,11. They reported that both nylon 11 and nylon 6,11 melt showed pseudoplastic and shear-thinning behavior. Zhuang et al.(Zhuang, Gui, Yang, Li, & Zhang, 1998) studied the rheological properties of reinforced nylon-66 composites. Gao et al.,(Gao et al., 1999) investigated the rheological properties of ABS-PA 1010 blends. They reported that the compatible ABS-PA 1010 blend has higher viscosity and lower crystallinity compared to the corresponding noncompatible blend.

The rheological behavior is the theoretical foundation for the polymer processing, such as extrusion, injection molding, and film production. In order to obtain the optimum conditions in an industrial processing and to obtain products with better properties, it is necessary to estimate the melt fluidity. The objective of the present work was to investigate the rheological behavior of polyamide 5,6 using parallel-plate rheometer to obtain information on the effect of temperature on the melt behavior of polyamide 5,6.

MATERIAL AND METHODS

Materials

PA5,6 pellets with an intrinsic viscosity of 0.68 dl/g were kindly supplied from Guangdong Xinhui Media Nylon Co. Ltd, China, synthesized from adipic acid and *1,5* bioengineering pentyl diamine, with a molecular weight of 18,000.

PA6 pellets were kindly supplied from Guangdong Xinhui Media Nylon Co. Ltd, China. Model: Bright R.V.2.4-2.8, with a molecular weight of 22000.

The samples were dried in a vacuum oven at 100 ^{0}C for 8 h. prior to the measurement to remove all moisture, which might influence the results.

Rheological measurements:

Rheological properties of PA 5,6 and PA6 were measured using a Haake Mars III parallel-plate rheometer from Thermo Scientific Company. Viscoelastic measurements were performed with disposable aluminum parallel plates 25 mm in diameter, with a gap thickness of 1.00 mm to get complex viscosity (η^*), the storage modulus (G'), and loss modulus (G"). Dynamic frequency sweep tests were executed in the frequency range of 0.1~100 rad/sec at various temperatures (285, 295, 300 ^{0}C). Before the measurements, the samples were prepared using injection molder at temperature 285 ^{0}C. All of the following results of the rheological characterization use Haake software for their analysis.

RESULTS AND DISCUSSIONS

The rheological properties of polymeric materials are important for optimizing the processing conditions such as extrusion, injection moulding and melt spinning, which are highly dependent on temperature, pressure, molecular weight and shear rate ("Guidelines for Rheological Characterization of Polyamide Melts (IUPAC Technical Report)," 2009). Polymer melts exhibit elastic as well as viscous properties. This is evident in the swell of the polymer melt upon emergence from the extrusion die, a behavior that results from the recovery of stored elastic energy plus normal stress effects. In this study the melt rheological measurements for PA 5,6 and PA 6 were carried out at temperatures between 285 and 300 ^{0}C in order to investigate the temperature effect on the rheological properties. The variation of storage modulus (G') as a function of frequency (ω) of PA 5,6 and PA 6 at different temperatures are shown in Fig. 1(a) and (b), respectively. It is apparent that the temperature has a significant influence on the rheological behavior of PA 5,6 and PA 6. From Fig.1 (a), which clearly indicated that the storage modulus (G') of PA 5,6 decreases with the increase of temperature. From Fig.1 (b), it is also observed that the storage modulus (G') of PA 6 decreases with temperature increase. On the other hand, all samples are featured by prominent typical increase in storage modulus (G') with increasing frequency, indicating a possible transition from viscous liquid to solid-liquid behavior. Fig.2 (a) and (b) show respectively the loss modulus (G") of the PA 5,6 and PA 6 at different temperatures as a function of frequency. From Fig. 2(a), the loss modulus (G") decreases with temperature increase. From Fig. 2(b), it is also observed that the loss modulus (G") of PA 6 decreased with increasing temperature. Also, it is observed that the loss modulus (G") of PA 5,6 and PA 6 gradually increases with increasing frequency. The differences reduce with the increase of temperature.

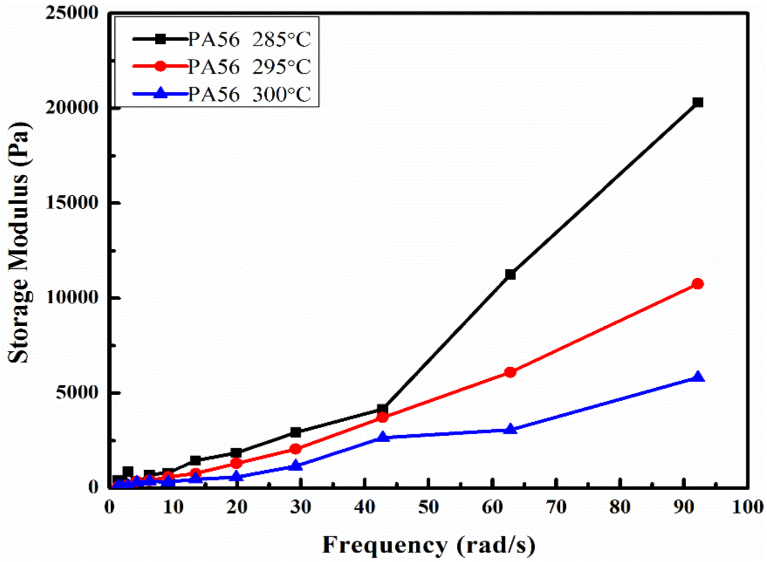

Figure 1(a): The frequency dependence of the storage modulus (G') for PA 5,6 at different temperatures

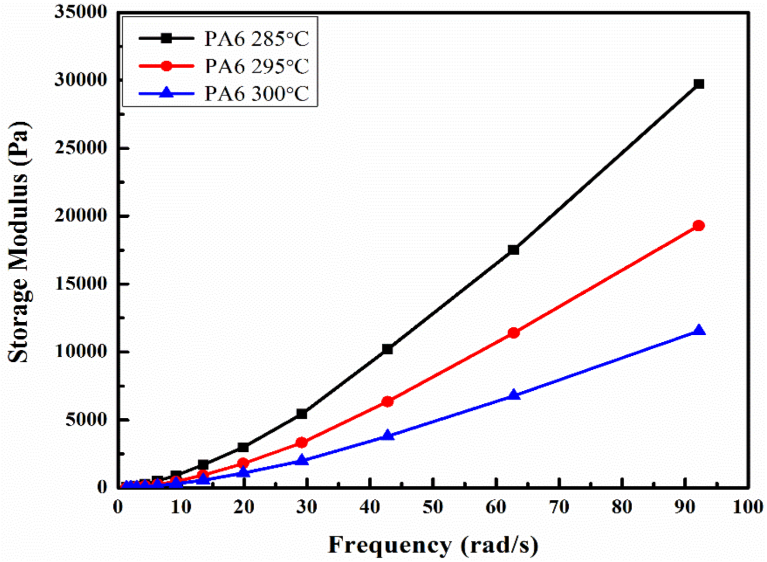

Figure 1(b): The frequency dependence of the storage modulus (G') for PA 6 at different temperatures

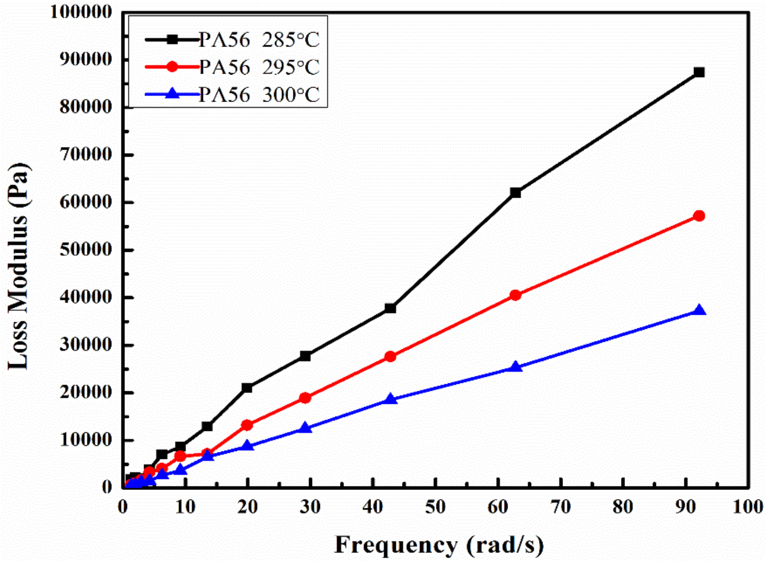

Figure 2(a): The frequency dependence of the loss modulus (G") for PA 5,6 at different temperatures

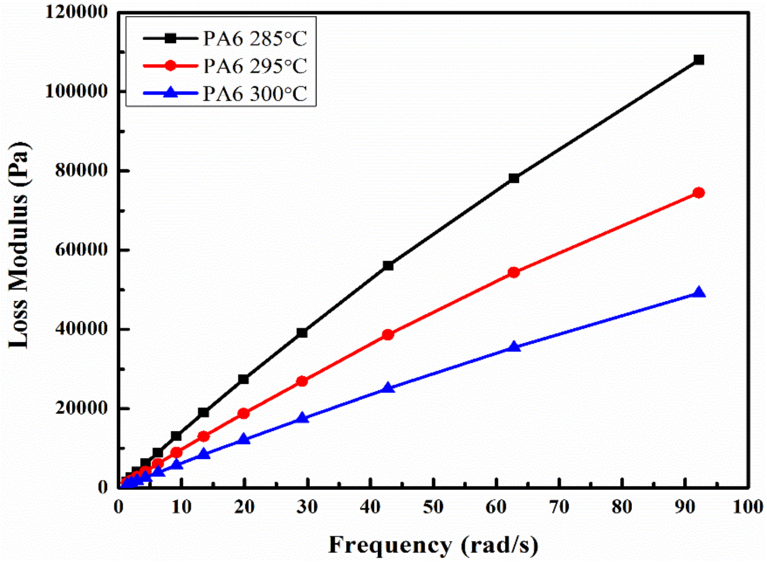

Figure 2(b): The frequency dependence of the loss modulus (G") for PA 6 at different temperatures

The frequency dependence of the complex viscosities (η*) for the PA 5,6 and PA 6 at various temperatures are presented in Fig.3 (a and b). It can be seen that the complex viscosities (η*) decreases with increasing the temperatures for both PA 5,6 and PA 6, indicating that the free volume of the PA 5,6 and PA 6 also increases with increasing temperature and results in decreased viscosity. For PA 5,6 Fig.3(a), the complex viscosity (η*) increases gradually under the frequency 0.1~10 rad/s, thereafter the frequency started to decrease slightly in the range of 10~20 rad/s, and then remains almost constant under the frequency range investigated (20~100 rad/s). However, with increasing the frequency the complex viscosity (η*) of the PA 6 Fig. 3(b) shows slight increase under the frequency between 0.1 and 10 rad/s, and then started to decrease with the frequency. Analyzing the reason complex viscosity decreases with increasing the shear rate, we believe that many polymeric liquids, melt, or solutions in solvents have long chain molecules in a random fashion loop and entangled with other molecules. These long chain molecules do not act alone in an empty space but millions of similar molecules inter-loop and entangle, leading to an intermolecular interaction. Non-permanent junctions are formed at entanglement points, leading to a wide chain network with molecule segments as connectors. When subjected suddenly to high shearing forces, the fluid will initially show a solid-like resistance against deformation within the limits of the chain network. In a second phase, the connector segments will elastically stretch and finally the molecules will start to disentangle, orient and irreversibly flow one over the other in the direction of the shearing force. The larger the shearing force, the more molecules will be disentangled; thus the apparent viscosity decrease is more obvious. For the PA 5,6 melt, the rebuilding of polymer chain entanglements can keep up with the destroying of the physically cross-linking sites at the shear force range, thus the viscosity remains almost constant showing a Newtonian behavior. On the other hand, the PA 6 melts, as the shear rate increases, the number of chain entanglements reduces, and the viscosity begins to decrease slightly with the shear rate increase consequently, it exhibits a much nearly Newtonian characteristics. Similar phenomenon was observed for other polyamides (Parrini et al., 1976). Parrini et al.(Parrini et al., 1976) reported that nylons exhibit a Newtonian behavior up to ~10^2 sec^{-1} and their pseudo-plastic behavior is very small.

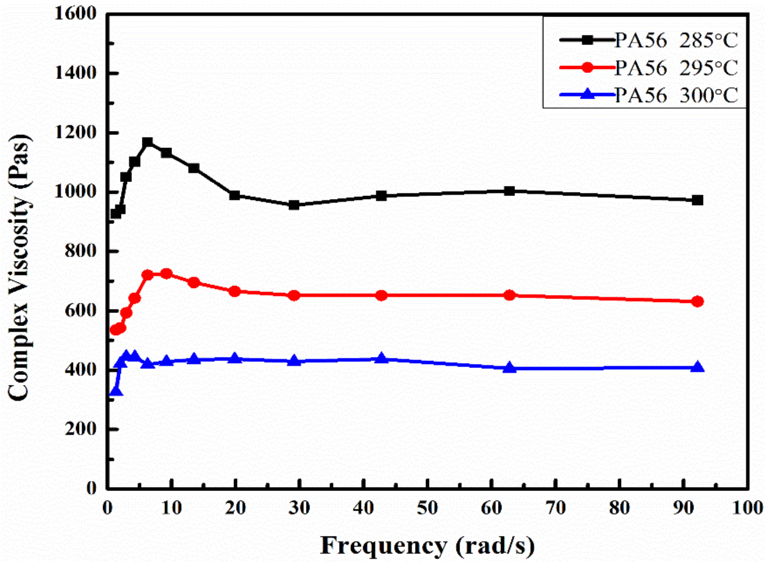

Figure 3(a): The frequency dependence of the complex viscosity (η*) for PA 5,6 at different temperatures

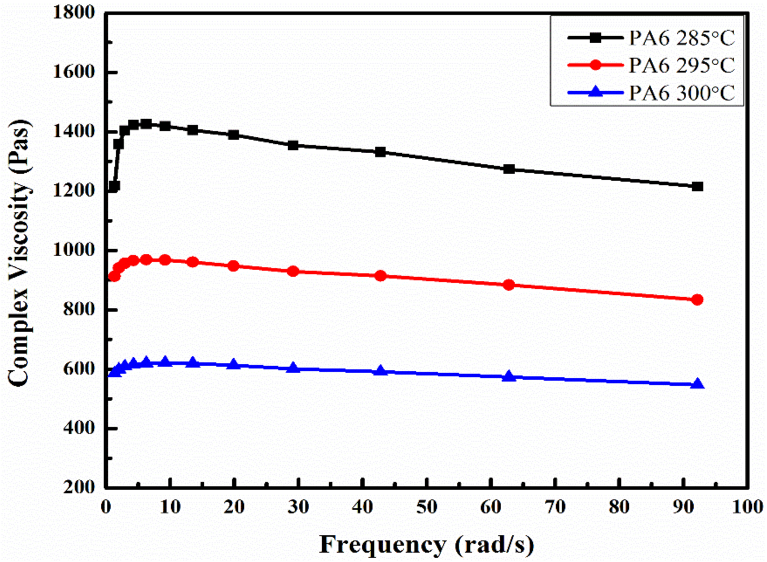

Figure 3(b): The frequency dependence of the complex viscosity (η*) for PA 6 at different temperatures

The rheological properties of polyamide 5,6 (PA5,6) have been studied by means of a Haake rheometer. The effect of temperature on the storage modulus, loss modulus, and complex viscosity was studied. The results showed that the complex viscosity, storage modulus, and loss modulus of PA 5,6 and PA 6 decrease with increasing the temperatures. It is worth noting that the complex viscosity of PA5,6 remained almost constant showing a Newtonian behavior, on the other hand, the complex viscosity of PA 6 slightly decreased with the increase shear rate exhibited a much nearly Newtonian behavior. Similar behavior was observed for other polyamides.

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