

Study of Rheological Property of Nylon-1212 with Haake Rheometer

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Abstract: Rheological properties of nylon-1212 have been studied by means of Haake Rheometer. The effect of shear rate and temperature on the apparent viscosity of nylon-1212 was discussed. A correlation of non-Newtonian index with the temperature was obtained. The results showed that the apparent viscosity decreases with the increase of the temperature. With increasing shear rate, shear thinning of nylon-1212 was observed clearly. From the relation of the temperature dependence of the polymer, we obtained the viscous flow activation energy. We conclude that the apparent viscosity is sensitive to temperature at lower shear stress because of higher viscous flow activation energy, and the temperature affect on the apparent viscosity becomes

weaker at higher shear stress because of lower viscous flow activation energy. We have investigated the creep and elastic recovery of nylon-1212. A creep test was carried out to define the linear viscoelastic range as 1.0 and 5.0 Pa for 195 and 190°C nylon-1212 melts, respectively. A time-dependent response was found for the creep and recovery phases at a lower applied shear stress. However, at higher shear stress, the creep and recovery phases were time-independent. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 379–385, 2003

Key words: nylon-1212; rheology; apparent viscosity; viscous flow; activation energy; creep and elastic recovery

INTRODUCTION

Linear aliphatic polyamides, commonly known 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, low creep and good temperature resistance that allow widespread use of this family of polymers as fibers and engineering thermoplastics.^{1,2} The attractive matrix of properties of polyamides originates in strong hydrogen bonds, which are formed by the amide groups.³ Since their discovery by Carothers in 1934,^{4,5} many nylons have been investigated, a number of which have been commercialized during the past 50 years.² Relatively little effort has been made to explore and investigate nylons that comprise longer alkane segments (\geq deodecane). The research of these nylons with long alkane segments might lead to a new field of nylons. The most important attributes of polyamides with long alkane segments are superb toughness, high tensile strength, abrasion resistance, dimensional stability, superb wet strength retention, and low tissue reaction.^{6–8} Long alkane segment nylons such as nylon-12 have been widely used in the military, machinery, electron equipment, automobile, information and aviation industries.^{9–12} Due to their anticipated amphiphilic character, these nylons might

find new applications as coatings, compatibilizers between, for example, nylons and polyolefin, as well as partially hydrophobic high-temperature engineering polymers, and biomedical applications such as skin closure, plastic surgery, ophthalmology, and microsurgery.

A literature review yields several reports that describe AABB nylons that comprise long aliphatic segments.^{13–17} But literature on poly(dodecamethylene dodecanoamide), which is called nylon-1212, is scarce. Jones et al.^{18,19} have focused on the crystal structure of nylon-1212. At room temperature, nylon-1212 exhibits both the α_p and β_p structures. Unit cell dimensions are as follows: α_p structures $a = 0.490$, $b = 0.521$, $c = 3.23$, $\alpha = 50$, $\beta = 77$, and $\gamma = 64$; β_p structures $a = 0.490$, $b = 0.802$, $c = 3.23$, $\alpha = 90$, $\beta = 77$, $\gamma = 67$. A new synthesis technique to synthesize nylon-1212 has been successfully developed at Zhengzhou University and industrialized by Zibo Guangtong Chemical Co. Ltd, China since 1998.

Rheological characteristics of polymer melts and polymer solutions are important for both processing and final-product quality. Therefore, the study of its melt rheology is of major importance.

The relatively low melt viscosity and high melting point of nylon resins can be compared to the previously available data on polyacrylates, polystyrenes, and polyvinyls. So, investigating the rheological properties of nylons is important. Bankar et al.²⁰ studied rheological properties of nylon-6 at different temperatures. Utracki, et al.²¹ investigated the melt rheology of high density polyethylene polyamide-6 blends.

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TABLE I
Physical Mechanical Properties of Nylon-1212

Physical properties	
η_r	1.82
Specific gravity (g/cm ³)	1.01
Melting point (°C)	185
Hardness (Rockwell)	103
Water absorption, 23°C, 24h (%)	0.25
Tensile strength (MPa)	56.1
Elongation at break (%)	370
Impact strength-notched (Charpy)(KJ/m ²)	16.1

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. Zhuang et al.²² studied the rheological properties of reinforced nylon-66 composites. Gao et al.²³ studied 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 properties in the molten state have received little study on nylons with long alkane segments. Knowledge of the rheological properties of nylon-1212 melt is important for the design, selection, and processes. In this article, we investigate the rheology of nylon-1212 using both parallel plate rotational viscometers and capillary rheometers to obtain information on normal stresses, and to study the behavior of nylon-1212.

EXPERIMENTAL

Polymers

Nylon-1212 was supplied by Zibo Guangtong Chemical Co. Ltd (China). The sample was dried for 24 hours prior to the measurements at 85–90°C to remove all moisture, which can influence the results.

Instrumentation

The rheometers used for these tests were a Haake-150 parallel-plate rheometer and a Haake-II capillary rheometer. To make the measurements the parallel-plate rheometer (Haake-150) applied the high temperature measuring system TC501, ceramic rotors and the electric plate heating system. The Capillary rheometer (Haake-II) (40 L/D) was used to measure the steady shear viscosity of nylon-1212. All of the following results for a rheological characterization use Haake software to analyze.

Measurements

The samples have been tested in Control Stress mode at different temperatures from 195°C to 240°C with

parallel plate sensor PP35 (ceramic shaft) and initial gap of 1.000mm.

The test results are always based on rmp values of the plate and on measuring the resulting torque values at the plate. The rheological values are calculated as follows (which are given in the Haake Manual for data calculation):

Shear stress τ

$$\tau = A \times Md \quad (1)$$

where Md is the torque, and A is the stress factor. The factor 'A' is calculated using the following equation, and It has the unit of inverse volume: $A = 2/\pi R^3$ where R is the Plate radius.

The shear rate ($\dot{\gamma}$) is calculated by:

$$\dot{\gamma} = M \times \Omega \quad (2)$$

where M is the shear factor, ω is the angular velocity or speed calculated by $(2\pi/60) \cdot n$. The n is the speed. $M = R/h$, where R is the plate radius and h is the gap between the plates. The apparent viscosity η_a is obtained from the relation:

$$\eta_a = \tau \dot{\gamma} \quad (3)$$

Capillary rheometer measurements were performed with a capillary rheometer (Haake-II capillary rheometer). The die was made of tungsten-carbide steel. To determine the temperature effect on melt viscosity, nylon-1212 was extruded at a wide range of shear stresses from 300Pa to 2500Pa at several temperatures: 210°C, 215°C, 220°C, 225°C, and 230°C.

The creep and recovery behavior was measured with a parallel-plate rheometer order stress-controlled conditions (Haake Rheo-Stress RS150). The diameter of the upper plate was 35 mm and the gap between two plates was 1.000 mm. A stress was applied to the upper plate by a technique of frictionless contact. The test consisted of two main parts - creep and elastic recovery. The applied stress ranged from 0.5 to 100 Pa. For initial conditioning, the nylon-1212 was maintained at presetting temperature for 200 s. Subsequently, the stress was instantaneously applied, removed after 120s, and recovery was monitored for 300 s. All the measurements were carried out at 190°C, and 195°C.

RESULTS AND DISCUSSION

Typical flow curves

Using the apparatus described, we determined the flow cures of nylon-1212 so as to acquire a greater knowledge of the rheological behavior of the material

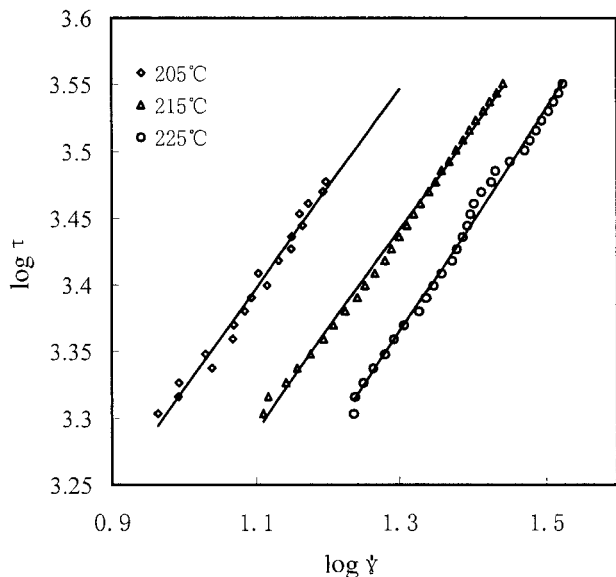


Figure 1 log τ vs log $\dot{\gamma}$ of nylon-1212 for different temperatures.

and to study its optimum use in the transformation processes.

Flow curves of nylon-1212 for 205°C, 215°C, and 225°C are shown in Figure 1. From this, we can see that with increasing temperature the curves decrease. That is to say, with the temperature increasing, the apparent viscosity of nylon-1212 is decreased. The curves deviate from Newtonian behavior, and nylon-1212 shows a non-Newton fluid rheological behavior. This is similar to many other nylons.^{24,25}

The Ostwald-de Waele or the "power-law,"²⁶

$$\tau = K \dot{\gamma}^n \tag{4}$$

is widely used as a model for non-Newtonian fluids, where τ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), K is a viscosity related constant, and n is an exponent (flow behavior index) that equals the slope of the log τ -log $\dot{\gamma}$ flow curve. For Newtonian fluids, $n = 1$; for dilatant fluids, $n > 1$; for pseudoplastic fluids, $n < 1$. From Figure 1, this slope can be determined by means of regression calculations using the "power-law" equation. We calculated the flow behavior index (n) at temperatures of 205°C, 215°C, 225°C, which is 0.747, 0.761, 0.832, respectively. The effect of the temperature on the flow behavior index is presented in Figure 1. From Figure 1, it is clear that the value of n is less than 1 for all temperatures under investigation, indicating the pseudoplastic nature of nylon-1212 in the molten state. With the increasing temperature the flow behavior index (n) enlarges, which indicates that the non-Newtonian behavior of nylon-1212 becomes weaker with increasing temperature. According to the time-temperature equivalence principle, increasing shear

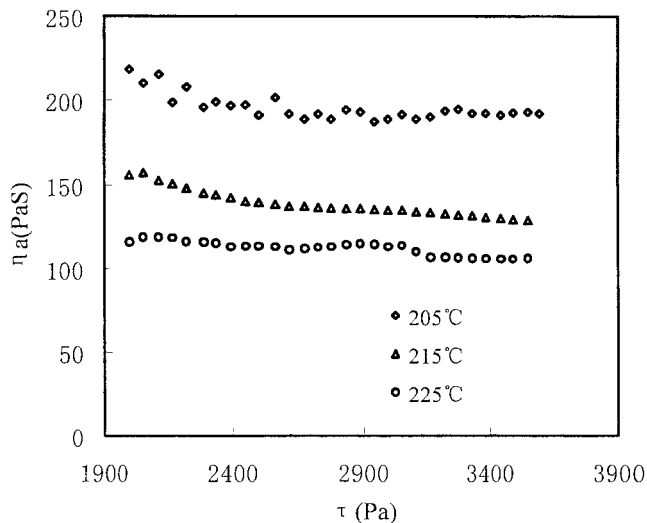


Figure 2 Apparent viscosity vs shear stress of nylon-1212 for different temperature.

rate and decreasing temperature are equivalent to polymer molecules' mobility, which is equivalent to the visco-elastic behavior. If one raises the temperature, the polymer molecular mobility is increased and the visco-elastic behavior become weaker; thus, the melt's non-Newtonian behavior becomes weaker. If conditions are reversed the melt non-Newtonian behavior becomes stronger.

The relationship between η_a and $\tau, \dot{\gamma}$

Figures 2 and 3 show the relationship between the apparent viscosity and the shear rate or shear stress. From Figures 2 and 3, we can understand that the

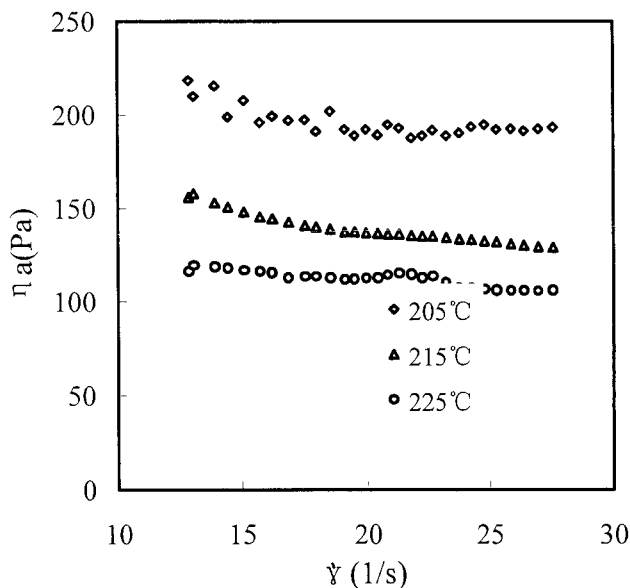


Figure 3 Apparent viscosity vs $\dot{\gamma}$ of nylon-1212 for different temperature.

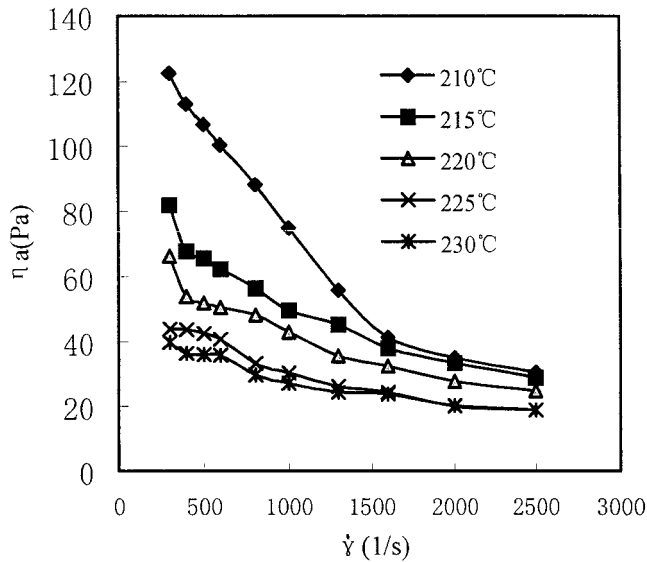


Figure 4 Apparent viscosity vs shear rate of nylon-1212 for different temperature (measurement with capillary rheometer).

apparent viscosity at different temperature is decreased with increasing shear rate or shear stress, which indicates nylon-1212's pseudoplastic flow behavior. Analyzing the reason η_a decreases with increasing τ or $\dot{\gamma}$, we believe that many polymeric liquids, melts, or solutions in solvents have long chain molecules which in a random fashion loop and entangle with other molecules. These long chain molecules do not act alone in an empty space but millions of similar molecules interloop 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;¹ thus the apparent viscosity decrease is more obvious.

Viscous flow activation energy

To indicate the sensitivity of the melt viscosity of nylon-1212 to temperature, the melt viscosity of nylon-1212 was measured at different temperatures with a capillary rheometer. Figure 4 shows the melt viscosity of nylon-1212 for different temperatures. From Figure 4, we can observe that at a low shear rate the apparent viscosity of nylon-1212 is decreased dramatically with the temperature increasing from 210°C to

220°C. From 220°C to 230°C, the apparent viscosity of nylon-1212 is decreased more slowly. The results may be due to the fact that, at low temperatures, the thermal energy environment supply approximately approaches or reaches the viscous flow activation energy, so the temperature affect on the apparent viscosity of nylon-1212 is great. But at high temperatures, the thermal energy exceeds the viscous flow activation energy of nylon-1212; thus, the temperature affect on the apparent viscosity is not obvious.

From Figure 4 we can also observe that the melt viscosity of nylon-1212 decreases with increased shear rate. This may be because, with the shear rate increasing and the shear stress enlarging, the macromolecules orient and irreversibly flow one over the other in the direction of the shearing force.

There are two well-known relationships to describe the temperature dependence of polymers: the Arrhenius and the WLF equations. The preferable model depends on the material, the temperature range of investigation, and the glass transition temperature. Just above the glass transition temperature (T_g), for example, the thermally stimulated flexibility of one polymer chain depends on its neighbors (known as a cooperative process). Well above T_g , the thermal flexibility of chains is less cooperative. This difference in the physical behavior requires a different mathematical description. But the melting points of nylons are over 100°C above their glass transition temperatures. At such a temperature increment above the glass transition temperature, nylons follow an Arrhenius relationship rather than a WLF relationship.²⁷ Therefore, the effect of temperature on viscosity is suitable to the Arrhenius' equation.

According to the Arrhenius' equation,

$$\eta_a = A^{(E_a/RT)} \quad (4)$$

$$\lg \eta_a = \lg A + \frac{1}{2.303} (E_a/R) \times 1/T \quad (5)$$

where η_a is the melt viscosity and E_a is the activation energy for the melt flow.

We made a plot of $\lg \eta_a - 1/T$ (Figure 5) and calculated the viscous flow activation energy according to the slope of the straight line. The results are shown in Table II. From Table II, we can see that the viscous flow activation energy is higher at lower shear stress; however, the viscous flow activation energy is much lower at higher shear stress. So, we can understand that the apparent viscosity is sensitive to temperature at lower shear stress because of higher E_a , and the temperature effect on the apparent viscosity becomes weaker at higher shear stress because of lower E_a .

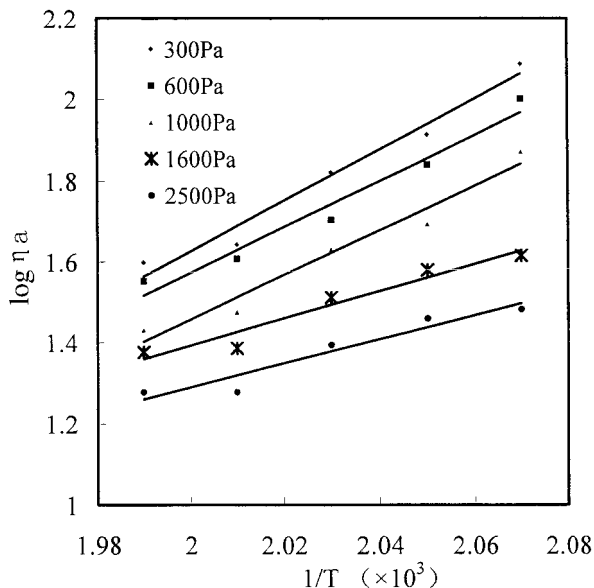


Figure 5 The temperature-dependence of apparent viscosity for nylon-1212.

Creep and elastic recovery

Creep is the test in which a constant stress is applied on a sample and the resulting strain is obtained. To reveal the viscoelastic characteristics of a polymer melt, a sample should be tested for its response to a constant stress over time. Polymer melts that exhibit viscoelastic behavior have long chain molecules, which at rest loop and entangle with each other at a minimum-energy state. Under deformation, these molecules stretch, increasing the bond vector angles and raising their energy state. If the cause of deformation is removed, molecules try to return to their original energy state. In pure elastic behavior, the deformation response to a constant shear stress (τ) is linearly linked to its value and is maintained as long as the stress is applied. The deformation will disappear completely when the stress is removed. A viscoelastic response to an applied constant stress varies with the time of application. Initially, the network of molecules undergoes deformation within the mechanical limits of the network. Continuous deformations lead to dismantling of the network and the polymer melt starts to flow. When the applied stress is removed, the total strain separates into a permanently maintained viscous part and a recovery elastic part. Viscoelastic behavior under lower values of stress usually has a linear response. In the range of nonlinear responses, at

TABLE II
Viscous Flow Activation Energy for Nylon-1212 Melt

Shear stress(Pa)	300	600	1000	1600	2500
E_a (KJ/mol)	119.69	108.01	105.41	64.34	56.87

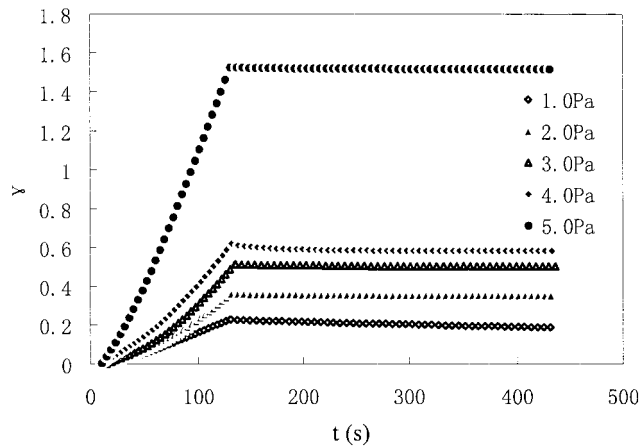


Figure 6 Creep and recovery curve of nylon-1212 at stresses from 1.0 Pa to 5.0 Pa at 190°C.

higher stress values, elasticity and viscosity data are usually dependent on the test conditions and the sensor system parameters.

Rheological systems that exhibit creep show a time-dependent strain $\gamma(t)$ under a constant stress τ , where²⁸:

$$\gamma(t) = J(t) \times \tau \tag{6}$$

The compliance, J (Pa^{-1}), of a sample is a material constant. The higher the compliance, the more easily the sample can be deformed by a given stress. In the linear viscoelastic range, the compliance is independent of the applied stress. Consequently, the proper creep and recovery test conditions within the limit of linear viscoelasticity can be defined. In addition, linear viscoelasticity is a nondestructive test of measuring the rheological behavior of a sample. The deforming energy is recovered when the applied stress is released. This indicates the network's ability to elastically deform while keeping intact.

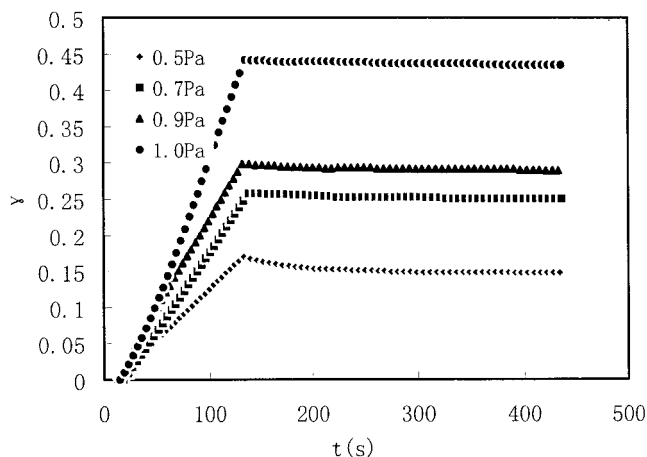


Figure 7 Creep and recovery curve of nylon-1212 at stresses from 0.5 Pa to 1.0 Pa at 195°C.

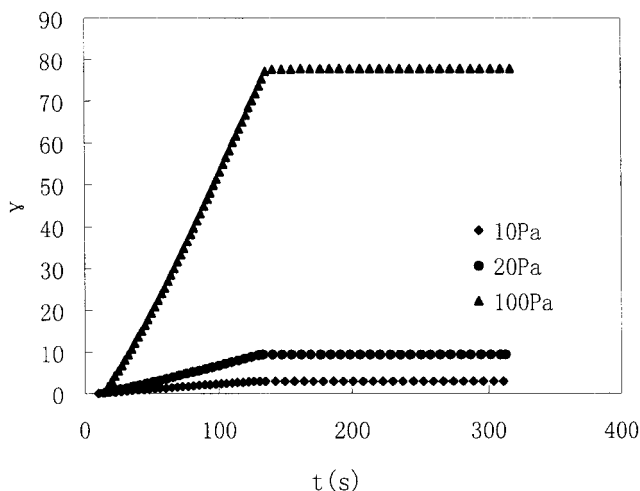


Figure 8 Viscous response of nylon-1212 melt in nonlinear viscoelastic range at 195°C.

In the creep-recovery test, it was important to initially define the linear viscoelastic range by applying different values of constant shear stress for 120 s. The strain data $\gamma(t)$ at different values of applied shear stress should coincide within the linear viscoelastic range. However, in the nonlinear viscoelastic range, the strain data curve separates significantly from the linear viscoelastic data. So, a creep test was carried out to define the linear viscoelastic range for the nylon-1212 melt. It was determined that the linear viscoelastic ranges for nylon-1212 at 190°C and 195°C were 5.0 and 1.0 Pa, respectively.

The creep-recovery experiments were conducted by applying a constant known value of shear stress to the sample using a parallel plate rheometer. The resulting strain was monitored as a function of time. The imposed stress was suddenly removed after 120 s, and recovery was monitored for 300 s. Figures 6 and 7 show the strain data $\gamma(t)$ for nylon-1212 at 190°C and 195°C with different values of applied shear stress. For nylon-1212, a noticeable time-dependent response is evident in the creep and recovery phases at lower applied shear stress. Therefore, nylon-1212 shows an elastic recovery in addition to its viscous response at lower applied shear stress. However, at higher applied shear stress, the time dependence in the creep phase is diminished and is significantly reduced in the recovery phase. The response of the strain (γ) to the instantaneous removal of stress can be summarized into three steps: Initially, a step reduction occurs as a pure elastic response, which is followed by an exponential decrease related to a viscoelastic response. Finally, the strain values approach a constant limit corresponding to the nonrecovered deformation of the viscous flow. For comparison, Figure 8 shows the strain values of nylon-1212 at 195°C for different shear stress values in the nonlinear viscoelastic range. Nylon-

1212 shows time-independent behavior in the creep and recovery phases. Also, a pure viscous response of nonrecovered deformation can be seen. This is significantly different from the behavior recovered in the linear viscoelastic range in Figures 6 and 7.

CONCLUSIONS

We studied the rheological properties of nylon-1212 by means of Haake Rheometer. The apparent viscosity of nylon-1212 is decreased with increases in the shear rate, shear stress and temperature. We obtained a correlation of non-Newtonian index with temperature. From the relation of the temperature dependence of the polymer, we calculated the viscous flow activation energy. We concluded that the apparent viscosity is sensitive to temperature at lower shear stress because of higher E_a , and the temperature effect on the apparent viscosity becomes weaker at higher shear stress because of lower E_a . We also investigated the creep and elastic recovery of nylon-1212. A creep test was carried out to define the linear viscoelastic range as 1.0 and 5.0 Pa for nylon melts at 195 and 190°C, respectively. A time-dependent response was found for the creep and recovery phases at a lower applied shear stress. However, at higher shear stress, the creep and recovery phases are time-independent.

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