Rheological Behavior of Semi-aromatic Transparent Polyamide

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ABSTRACT: The rheological behaviors of semi-aromatic transparent polyamide (SATPA) melt are investigated using a capillary rheometer. The effects of shear rate, shear stress, and temperature on the apparent viscosity η_a of SATPA are discussed. A correlation of non-Newtonian index with temperature is obtained. The results show the shear thinning of SATPA; meanwhile η_a decreases with increasing temperature and shear rate, and the viscous flow activation energy is further obtained from temperature dependence of the samples. It was concluded that the apparent viscosity η_a is sensitive to temperature at lower shear rate owing to the higher viscous flow activation energy; on the contrary, the influence of temperature effect on the apparent viscosity becomes minor at higher shear rate due to the lower viscous flow activation energy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1586–1589, 2005

Key words: semi-aromatic transparent polyamide; nylon; melt; rheology; transparency; amorphous

INTRODUCTION

Polyamide, generally known as nylon, is an important family of industrial materials for its prominent properties such as relatively high strength, good toughness, abrasion resistance, and good processability. These attractive properties of nylon originate mostly from the strong interchain hydrogen bonds formed between neighboring amide groups.[1] Many nylons have been developed and are now widely used in many fields such as machinery and chemical communication industries, since their synthesis by Carothers[2] in 1938. But the drawbacks, such as their low transparency, high water absorption, and relatively low impact strength at low temperature or in dry circumstances limit its application.[3] On the other hand, transparent polyamide has attracted more and more attention in recent years,[4–6] owing to its outstanding integrated properties including good transparency, superb toughness, high thermal stability, high impact strength, good resistance to aging, good resistance to hydrolysis, low water affinity, and good dimensional stability in the presence of moisture. For this reason, it has been widely used in delicate optical instruments, observation mirrors, gauge boards, athletic equipment, and so on.[3] It's reasonable to say that the research of transparent nylons might lead to a new field of polyamides. According to the constituent monomers, transparent polyamide can be classified as fully aliphatic, fully aromatic (polyaramid), and aliphatic–aromatic polyamide (that is semi-aromatic transparent polyamide, SATPA).[3] As of today, there are some patents describing the manufacture of transparent polyamide.[7–11] "Trogamid T" [poly(trimethyl hexamethylene terephthalamide)], with good rigidity, low thermal expansion coefficient, good thermal resistance, and insulating properties,[12] is the transparent polyamide that was first developed and commercialized by Dynamit Nobel Co.[13] But its trimethyl hexamethylene diamine (as a main monomer) is expensive.

SATPA has successfully developed using terephthalic acid, *m*-phthalic acid, and aliphatic diamines at Zhengzhou University by means of polycopolycondensation and industrialized by Pingdingshan Plastics Co. Ltd., China, since 2001.[14] This amorphous[its amorphous morphology had been proved by differential scanning calorimetry (DSC), polarized light microscopy (PLM), and wide- angle X-ray diffraction (WXRD)],[15] colorless material is exceptionally transparent (90%). The polymer is tough and resistant to scratching and abrasion and to attack by chemicals and solvents. Its high glass transition temperature (102°C) leads to a high Vicat softening temperature (120°C) and excellent retention of its mechanical properties at elevated temperatures (the main characteristics of SATPA are shown in Table I).

MI[a] (g/10min)	η_r[b]	Transparency (%)	Tg (°C)	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength-notched(Izod) (kJ/m^2)
1.84	2.3	90	102	96.26	78.10	5.35

[a] Measured at 235°C and loaded 2160 g.
[b] Solvent: concentrated sulfuric acid at 25°C.

However, a comprehensive study concerning its other properties is still lacking, at least in the published literature. The properties of polymer melts and polymer solutions are important for both processing and final-product quality. Unfortunately, for transparent polyamide little has been done with respect to its rheological properties in the molten state. To obtain materials with better physical and processing properties, it is important to understand the rheological behaviors of SATPA. In this article, we investigate the rheology of SATPA using a capillary rheometer to obtain information on normal stresses.

EXPERIMENTAL

Polymers

SATPA was supplied by Pingdingshan Plastics Co. Ltd., China. The sample was dried for at least 16 h at 85–90°C to remove moisture, prior to the following measurements.

Measurements

The rheometer used for the tests was a Haake-II capillary rheometer (Germany). The die was made of tungsten-carbide steel. This capillary rheometer (40L/D) was used to measure the steady shear viscosity of SATPA, and the curves were obtained by the software(supported by Haake-II capillary rheometer).

To determine the temperature effect on melt viscosity, SATPA was extruded at several temperatures: 160,170,180,190,200,210, and 220°C.

RESULTS AND DISCUSSION

Typical flow curves

Flow curves of transparent PA for 160, 170, 180, 190, 200, 210, and 220°C are shown in Figure 1. As indicated, lgτ decreases with increasing flow temperature, i.e., SATPA decreases with elevated temperature. This deviation from Newtonian behavior has been found in other sorts of nylons.[16,17]

The Ostwald-de Waele law, or the "power-law",[18] is widely used for non-Newtonian fluids, where τ is shear stress (Pa),

$$\tau = K\gamma^n, \qquad (1)$$

γ is shear rate(s^{-1}), K is a viscosity related constant, and n (flow behavior index) is an exponent that equals the slope of the logτ −logγ flow curve. For Newtonian fluids, $n = 1$; for dilatant fluids, $n > 1$; for pseudoplastic fluids, $n < 1$.

From Figure 1, using the equation (2),

$$n = \frac{d \lg \tau_{ap}}{d \lg \gamma_{ap}}. \qquad (2)$$

The effect of temperature on flow behavior is presented in Figure 2 in which n (flow behavior index) values are plotted as function of ln γ_{ap}. From Figure 2, it is evident that the value of n is less than 1 for all temperatures under investigation, implying the pseudoplastic nature of SATPA in the molten state. The increased n values with increasing temperature suggest the weakened non-Newtonian behavior of the samples. According to the time–temperature equivalence principle, increasing shear rate and decreasing temperature are equivalent to polymer molecules' mobility. Therefore, in this case, this principle is applicable to depict the viscoelastic behavior. In other words, if the temperature is raised, the polymer molecular mobility is more activated and the viscoelastic behav-
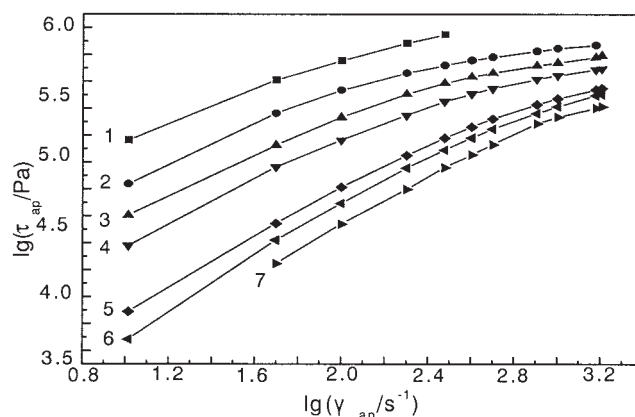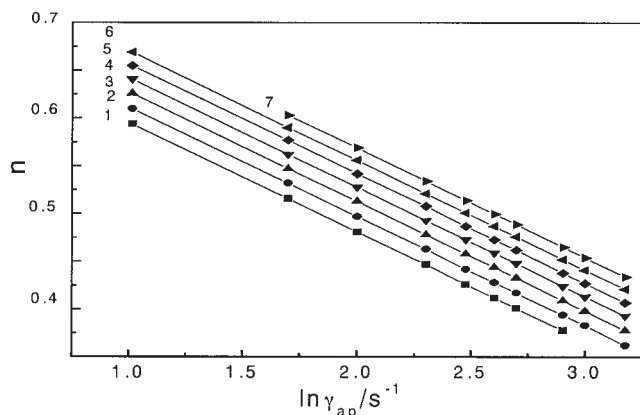

Figure 1 lgτ_{ap} versus lgγ_{ap} of SATPA at different temperatures.1, 160°C; 2, 170°C; 3, 180°C; 4, 190°C; 5, 200°C; 6, 210°C; 7, 220°C.
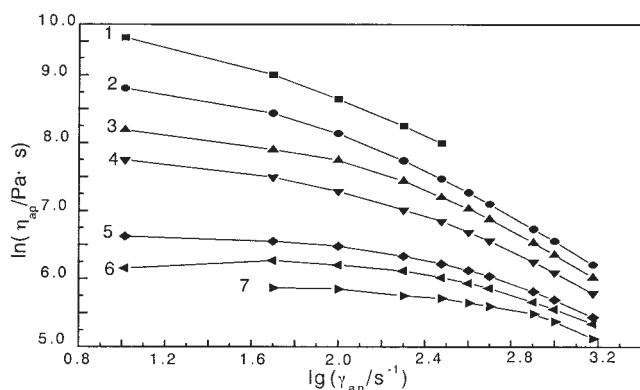
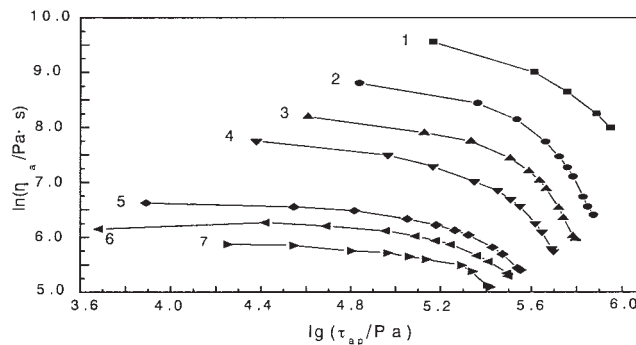**Figure 2** Flow behavior index (n) versus ln γ_{ap} of SATPA. Temperatures are the same as in Figure 1.

ior become weaker; thus, the melt's non-Newtonian behavior is accordingly weaker.

The relationship between η_a and τ_{ap}, γ_{ap}

Figures 3 and 4, respectively, show the relationship between the apparent viscosity η_a and the shear rate γ_{ap} or shear stress τ_{ap}. From Figures 3 and 4, it can be understood that apparent viscosity η_a at different temperature is decreased with increasing shear rate or shear stress, which indicates transparent PA's pseudoplastic flow behavior. The reason is 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. Nonpermanent junctions are formed at entangle 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.

The relationship between η_a and temperature

In Figure 5, the melt viscosities of SATPA are plotted as a function of the temperature ($1/T$). As indicated, the apparent viscosity of SATPA is decreased with the temperature at a fixed shear rate. There are two empirical relationships to describe the temperature dependence of polymeric systems: the Arrhenius and the WLF equations. In this case, which with the temperatures well above the T_g (about 100°C) of the samples, the Arrhenuis equation (see Eq. (3)) is more suitable to depict the movement, where η_a is the melt viscosity and ΔE is the activation energy for the melt flow.

$$\eta_a = A \exp (\Delta E / RT) \tag{3}$$

Figure 4 Apparent viscosity versus shear stress. Temperatures are the same as in Figure 1.

Figure 3 Apparent viscosity η_a versus shear rate γ_{ap}. Temperatures are the same as in Figure 1.

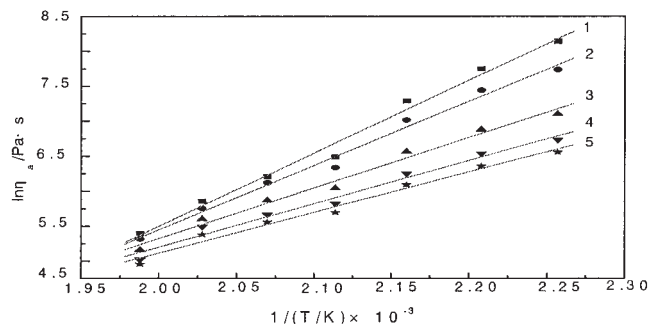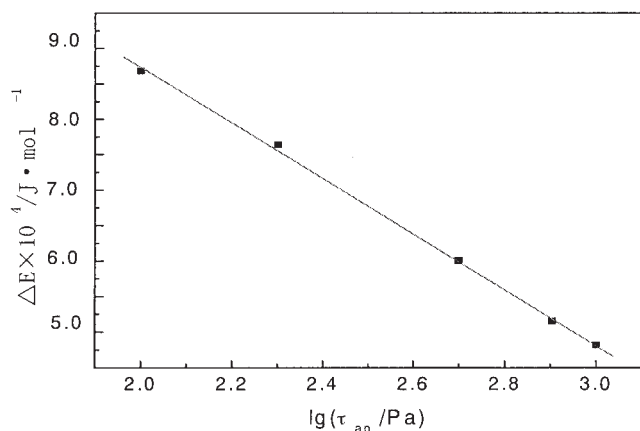**Figure 5** The temperature dependence of apparent viscosity 1, 100 s^{-1}; 2, 200 s^{-1}; 3, 500 s^{-1}; 4, 800 s^{-1}; 5, 1000 s^{-1}.

Figure 6 Viscous flow activation energy ΔE versus $\lg\tau_{ap}$

Accordingly, for all temperatures investigated, the viscous flow activation energy could be obtained by calculating the slope of the each line in Figure 5. Further, these activation energy values are plotted as a function of $\lg\tau_{ap}$ (like Fig. 6). As presented, the viscous flow activation energy is higher at lower shear rate; however, the viscous flow activation energy is much lower at higher shear rate. The apparent viscosity is more sensitive to temperature at lower shear rate because of higher ΔE, and the temperature effect on the apparent viscosity becomes weaker at higher shear rate because of lower ΔE.

CONCLUSIONS

The rheological properties of SATPA were studied by means of a Haake rheometer. SATPA's melt is pseudoplastic in nature. The apparent viscosity of SATPA is decreased with increase in the shear rate, shear stress, and temperature. A correlation of the non-Newtonian index and viscous flow activation energy with temperature was obtained, respectively. It can be concluded that apparent viscosity is sensitive to temperature at lower shear rate because of higher ΔE, and the effect of temperature on the apparent viscosity becomes weaker at higher shear rate because of lower ΔE.

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