Rheological Behavior of Polyamide 11 with Varying Initial Moisture Content

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ABSTRACT: The rheological behavior of polyamide 11 samples with different initial moisture levels is investigated. More specifically, the time evolution of the linear viscoelastic properties is monitored at a given frequency. The time dependence of these properties is exponential in time, reflecting postcondensation reactions in the samples. The crossover time, at which the storage modulus and loss modulus intersect, can be used as a characteristic timescale for the reaction. This crossover time and the corresponding complex viscosity can be used as fingerprints of the material, reflecting the moisture content in the material. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 666–670, 2005

Key words: nylon; processing; rheology

INTRODUCTION

The knowledge of the appropriate rheological behavior of a material is a fundamental prerequisite for processing it in a controlled manner. However, sometimes the measurement of the flow properties can be hampered by the sample's reactivity and environmental conditions. Notorious in this respect are condensation polymers such as polyesters and polyamides. The major difficulty in characterizing the flow properties of these materials is due to their hygroscopic nature; that is, the rheological data depend to a large extent on the initial moisture level of the polymer. High moisture levels can lead to degradation and foaming, whereas relatively low levels of moisture can act as a plasticizer in, for example, polyamide 6 (PA6) during processing.[1]

Although the hydrophilic nature of such polymers is known, studies on the effect of moisture on the rheology and processing of such polymers are hardly documented in the literature. Seo and Cloyd[2] studied the effect of moisture on the viscosity of poly(ethylene terephthalate). They showed that the aging of the polyester melt consisted of two contributions: an initial fast degradation, attributed to hydrolysis, and a rather slow degradation, attributed to thermooxidative degradation. Laun[3] showed that PA6 melts were not stable because of the chemical nature of the macromolecules: depending on the initial moisture content, a new condensation equilibrium could be reached. Pezzin and Gechele[4] studied the melt stability of PA6 samples with various degrees of humidity. They observed that the melt viscosity increased with time for samples with a low water content, whereas it decreased with time for higher humidity values. Khanna et al.[1] investigated the effect of the drying time on the melt viscosity. They concluded that changing the moisture content from 0.1 to 0 wt % led to a sharp increase in the zero-shear viscosity, the effect being completely reversible.

The aforementioned investigations clearly indicate that controlling the humidity is of the utmost importance if one wants to process nylon plastics properly. Therefore, most resin suppliers recommend that, before the processing of nylons, the pellets should be dried to small moisture levels and that the plant environment conditions should be under strict control. Knowledge of the humidity level is therefore a prerequisite before processing, and typically this moisture content is measured by means of a Karl Fischer titration (e.g., see ref. 5.)

In this article, we elucidate the effects of various moisture contents on the rheological behavior of a commercial polyamide 11 (PA11). This resin is often used in flexible pipe applications for offshore oilfield exploration. Because of the high hydrocarbon proportion of the repeat unit, the typical water absorption characteristics of PA11 are greatly reduced in comparison with those of PA6 and polyamide 6-6. Nevertheless, the processing behavior of the polymer still depends to a large extent on the initial moisture content. However, to the best of our knowledge, no systematic

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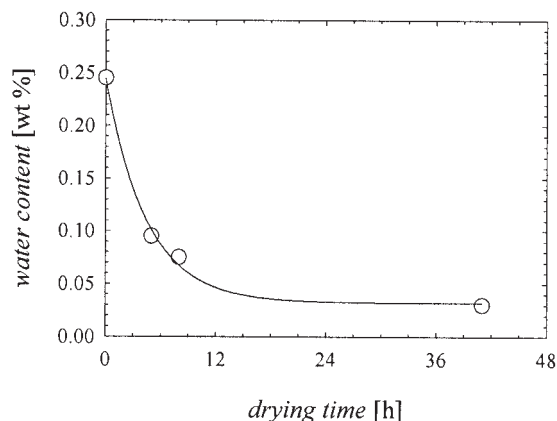
Figure 1 Water content of PA11 (from Karl Fischer titration) versus the drying time. The samples were dried at 80°C and 10 mbar.

studies on the rheological behavior of PA11 have been published in the literature.

EXPERIMENTAL

Materials

The model material used for this study was a commercial grade of PA11, Rilsan B, produced by Atofina (Serquigny, France). The nominal melting temperature, defined as the peak in a DSC endotherm during the second heating at a constant rate of 10 K/min, was 189°C. The structural formula of PA11 is as follows:

$$[\text{N} - \overset{\text{H}}{\underset{|}{}} - \overset{\text{O}}{\underset{\|}{\text{C}}} - (\text{CH}_2)_{10}]$$
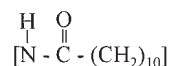
To produce samples with different initial moisture contents, we conditioned polymer pellets in a vacuum oven at approximately 10 mbar and 80°C for different drying times (0–41 h). Subsequently, the water content was determined by Karl Fischer titration. Figure 1 shows the weight percentage of water as a function of the drying time. The starting value, 0.245 wt %, represents the moisture of the samples exposed to the laboratory atmosphere. The water content after a 12-h conditioning fell below 0.05 wt %, which is normally considered a limiting value for rheological measurements.[5]

Methods

Rheological experiments were carried out with an SR-200 stress-controlled rotational rheometer from Rheometric Scientific. Viscoelastic measurements were performed with disposable aluminum parallel plates 25 mm in diameter, with a gap thickness of 1 mm, under

a dry nitrogen atmosphere. The electrically heated plate configuration was used for temperature control.

Small-angle oscillations were used to follow the evolution of the viscoelastic properties during isothermal tests at 210, 230, and 250°C at a frequency of 1 rad/s. For all the experimental conditions, it was always verified that the measuring time for a single data point was short enough so that the viscoelastic properties of time-changing samples did not significantly vary during individual measurements. A stress amplitude of 200 Pa was used for all tests, and it was verified that the corresponding oscillation amplitude was small enough not to influence the observed phenomena. Each test was repeated at least three times to check reproducibility.

To measure the rheological characteristics of time-changing samples such as the nylons used in this work, a well-controlled experimental protocol needed to be established. At time zero, predried polymer pellets (as described in the Materials section) were loaded onto the rheometer plate, which was already at the experimental temperature. Subsequently, the gap was lowered to the measuring gap, which was reached after approximately 90 s. No data points were collected during this first time period. No disk-shaped samples were prepared to perform the rheological measurements. This was done on purpose because the pressing operation would have affected the water content and hence would have made the initial water content unknown.

RESULTS AND DISCUSSION

Evolution of the linear viscoelastic properties

Typical experimental results are shown in Figure 2, which presents the time evolution of the complex viscosity (η^*), storage modulus (G'), and loss modulus (G'') at 210°C for a sample with an initial water content
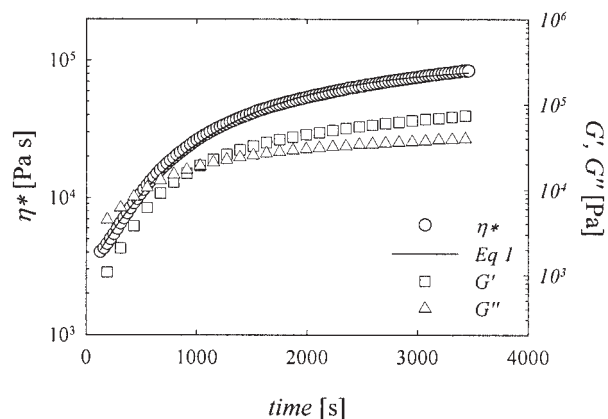

Figure 2 Time evolution of η^* (on the left axis) and G' and G'' (on the right axis) at 210°C. The initial moisture content was 0.095 wt %. The solid line represent eq. (1) (see the text).

of 0.095 wt %. Zero of the timescale corresponds to the moment at which the pellets are loaded on the rheometer plates. As already stated previously, no data points were collected during the first 90 s, the time necessary to reach the measurement gap. An inspection of Figure 2 shows that η^* and the viscoelastic moduli increase with time; this reflects a postcondensation reaction of the material that leads to an increasing molecular weight. The observed evolution of the linear viscoelastic properties clearly reflects the bulk behavior in the material, and it is not a mere edge phenomenon. To verify this idea, we conducted the following experiment: the measurement of the moduli was interrupted, a steady shear rate was applied, and after some time the measurement of the moduli was resumed. If an edge phenomenon had been present, the application of the shear flow would have modified the edge and led to different moduli, with respect to the values before the shearing was started. However, because the shearing operation did not alter the evolution of the moduli, we certainly observed a bulk-related event. In addition, it has been verified that the time evolution of the rheological properties is gap-independent.

To quantitatively describe the evolution of the viscoelastic properties, we use the crossover time t_x (defined as the time at which G' and G'' intersect) as a characteristic kinetic parameter. The η^*–time data have been fitted with an exponential function:

$$\log \eta^* = \log \eta_0^* + a(1 - e^{-t/t_x}) \qquad (1)$$

where η_0^* is the complex viscosity at time (t) equal to zero; a represents the logarithmic viscosity increase; and t_x is the characteristic time constant, which has been pegged to the crossover time.

For the analyzed PA11, t_x at the frequency of 1 rad/s is a close approximation of the gel time, defined as the instant at which the loss angle is frequency-independent.[6] In this view, t_x not only is a reliable fitting parameter but also has a clear physical meaning: it marks the transition between liquidlike and solidlike behavior.

Equation (1) is a purely empirical equation used to describe our experimental data, but nevertheless it has some physical meaning, as pointed out later in the discussion.

The viscosity increase is related to a molecular weight increase—for instance, the zero-shear viscosity increases with a 3.4 power of the molecular weight[7]— because of a further polycondensation of PA11. The polycondensation of nylons is a reversible reaction between amine groups and carboxylic groups that produces amide linkages and water. The equilibrium is regulated by a thermodynamic constant, but high molecular weights can still be obtained by the removal of water. Normally, the reaction is acid-catalyzed, and

polymer end groups are not terminated. The presence of these unterminated end groups and catalyst traces means that the actual molecular weight can easily change; this process is a function of the moisture content. Indeed, if the amount of water is less that that prescribed by the thermodynamic equilibrium constant, the reaction proceeds toward further condensation, and the molecular weight increases. If the amount of water is more than the equilibrium value, the reaction goes in the direction of hydrolysis, and consequently, the molecular weight decreases. Normally, second-order kinetics (first-order in both amine and acid groups) describe satisfactorily the polycondensation of PA11 in the melt phase.[8,9] Variations in the melt viscosity can therefore be used to monitor changes in the molecular weight. In particular, second-order kinetics lead to single exponential growth for the viscosity.[2] This exponential growth is experimentally observed (see Fig. 2) and predicted by eq. (1) up to time t_x. Beyond t_x, when the system is solidlike, the kinetics dramatically slow down because of the high molecular weight and are controlled by the diffusion of the reactive end groups.[8]

Effect of the initial moisture content and temperature

Now that we have defined the relationship between the evolution of the linear viscoelastic parameters and the continuous polymerization of PA11, it is important to know how the initial moisture content and the measurement (or reaction) temperature influence the rheological response. Therefore, the time evolution of the viscoelastic properties has been monitored at three temperatures (210, 230, and 250°C) and at four moisture levels (0.03, 0.075, 0.095, and 0.245 wt %).

As already shown in Figure 2, η^* and the viscoelastic moduli increase with time for the investigated temperatures and initial moisture levels. This behavior, as already observed by Pezzin and Gechele[4] for PA6, depends on the initial moisture content. The first set of results (see Fig. 3) shows η^*–time curves at 230°C and at four different water contents.

The collection of data starts after approximately 90 s. The initial value of η^* [η_0^* in eq. (1)] strongly depends on the moisture content: the lower the moisture level, the higher the viscosity. This result is expected because the water molecules act as plasticizers, reducing hydrogen-bonding interactions among polyamide chains. As shown in Figure 3, all curves increase as a function of time. The increase is faster in the initial stages, then slows down, and eventually stops as an equilibrium is reached. Moreover, a dependence of the kinetics on the moisture content can be observed: as the water content decreases, the kinetics become faster. This is clearly shown in Figure 3 with decreasing t_x.
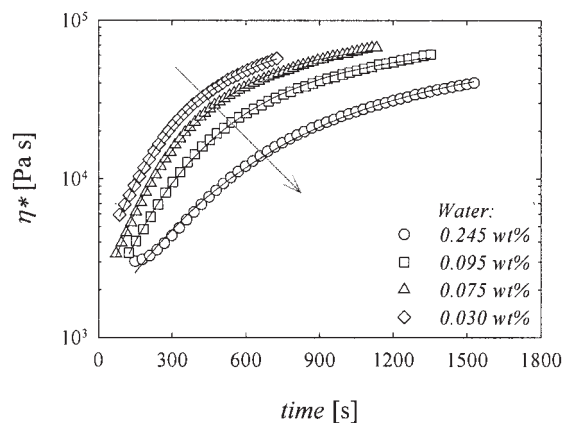
Figure 3 Evolution of η^* at the experimental temperature of 230°C. The different symbols refer to different moisture contents. The lines are data regressions with eq. (1), for which the time constant has been fixed equal to t_x. The arrow points in the direction of increasing moisture.

The water content not only determines the equilibrium composition and viscosity but also regulates the kinetics. Indeed, the lower the water content is, the lower the hydrolysis rate is and consequently the higher the net formation rate is of amide linkages.

Establishing a direct correlation between the kinetics of polymerization and the evolution of viscoelastic properties would require more effort: it is not the purpose of this work, but this is the objective of what is usually called rheokinetics.[10]

Next to the initial moisture level, the temperature is expected to play an important role in the postcondensation reaction, and hence studying its effect on the rheology is of relevance to understanding the processing behavior of PA11. Figure 4 reveals the effect of temperature on the time evolution of η^*, with the moisture content kept fixed at 0.095 wt %. As the
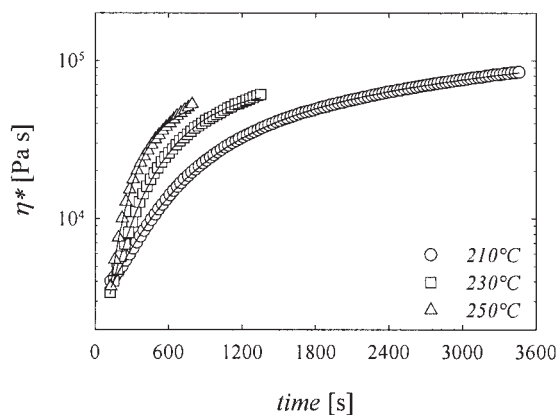

Figure 4 Evolution of η^* with 0.095 wt % moisture. The different symbols refer to different temperatures. The lines are data regressions with eq. (1), for which the time constant has been fixed equal to t_x.
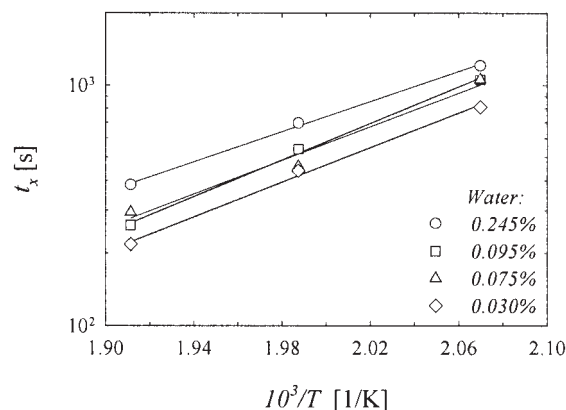

Figure 5 t_x versus the reciprocal of the absolute temperature $(10^3/T)$. The different symbols refer to different moisture contents. The lines are Arrhenius fits.

temperature is increased, the evolution becomes faster as a result of faster polycondensation kinetics, and t_x correspondingly decreases. The relative positions of the different curves are dictated by the relationship between the effects of water on the rheological behavior of PA11 and on its polycondensation kinetics.

The temperature dependence of the gel (or crossover) time is shown in Figure 5, where t_x is plotted versus the reciprocal of the absolute temperature. For each moisture content, t_x decreases with temperature in an Arrhenius-like fashion. Data regression gives the activation energies for each moisture content. The activation energies are very similar for all the samples, with an average value of 67 kJ/mol. This value substantially agrees with the value of 62.2 kJ/mol reported for the second-order kinetic constant of a similar polyamide by Blondel et al.[9] This is further confirmation that t_x is a good characteristic kinetic parameter for following the postcondensation kinetics of nylon. In addition, the activation energy does not depend on the initial moisture consent. Hence, it can be concluded that the change in the viscoelastic properties is merely due to the polymerization of the nylon: a possible contribution of water diffusion can, in the moisture range used in this work, be neglected.

Isomoisture experiments versus isothermal experiments

Initially, a temperature increase has apparently the same effect as a moisture decrease because they both lead to faster kinetics. Despite the similar effects that both a moisture decrease and a temperature increase have on an overall kinetic parameter such as t_x, the analogy cannot be complete. For instance, η_0^* increases as the moisture decreases, whereas it decreases as the temperature increases. Furthermore, viscosity–time curves (with a fixed temperature and a moisture pa-
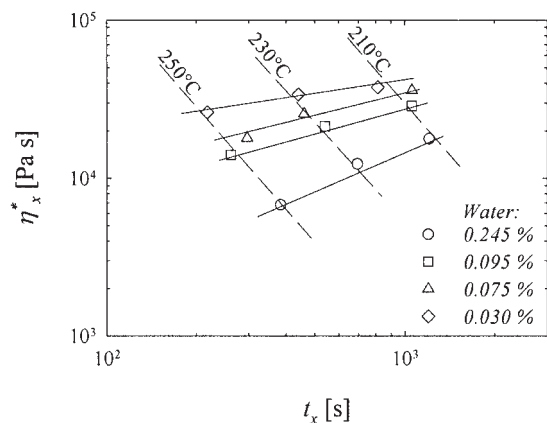
Figure 6 η_x^* versus t_x. The different symbols refer to different moisture contents. Two families of lines have been drawn to guide the eye: the solid lines are isomoisture lines, and the dashed lines are isothermal lines.

rameter; see Fig. 3) never intersect; whereas curves with a fixed moisture and a temperature parameter do intersect, as the highest temperature corresponds the lowest initial viscosity but the highest kinetic constant.

With the temperature fixed, there is a unique relationship between t_x and the moisture content; as the moisture content decreases, t_x decreases. However, if the constraint of the fixed temperature is removed, the same reduced t_x value can be achieved by either a moisture decrease or a temperature increase. In general, there is not a unique relationship between the moisture content and t_x. However, polymers at the crossover point are characterized by (at least) two parameters: t_x and its corresponding η^*.

When the complex viscosity at the crossover point (η_x^*) is plotted as a function of the gel time, we obtain the graph shown in Figure 6. Two distinct families of lines have been drawn: isomoisture lines (solid) and isothermal lines (dashed). An inspection of Figure 6 provides a more complete view of what happens when the temperature and moisture content are changed. As the temperature is raised with constant moisture, we move along one of the solid lines; both t_x and η_x^* decrease. However, as the moisture decreases at a fixed temperature (we are now moving along one of the dashed lines), t_x still decreases, whereas η_x^* increases.

Figure 6 has an additional advantage: it is possible to extract information about the unknown moisture content of a sample through the knowledge of its crossover point. Once a graph like Figure 6 has been prepared and calibrated with known moisture contents from Karl Fisher titration, linear interpolation is possible between two adjacent isomoisture lines to obtain an estimate of the sample's moisture content. Although this might seem a cumbersome procedure, it

still has its merits in a laboratory environment because a simple rheological test (e.g., using pellets that have been stored for a long time) can yield information about the condition of the sample and can give a fast response concerning whether the sample needs some preconditioning before further handling.

CONCLUSIONS

In this article, the rheological properties of PA11 have been studied at various initial moisture levels. PA11, even at temperatures slightly higher than the melting point, shows an exponential increase in its viscoelastic properties with time. This increase can be attributed to postcondensation reactions that increase the molecular weight. The evolution of the viscoelastic properties can be modeled with a single exponential function reflecting second-order reaction kinetics; this is consistent with the literature. The exponential fit uses an experimentally determined timescale, namely t_x, defined as the time at which G' and G'' intersect. In addition, a decreasing moisture content leads to a faster evolution of the viscoelastic properties and, consequently, to a lower t_x value. t_x follows an Arrhenius law as a function of temperature, and the resulting activation energy is independent of the initial moisture content. When η_x^* is plotted as a function of t_x, all data fall on two distinct families of lines: isothermal and isomoisture. Such a graph represents a fingerprint of the material and can be used to estimate the moisture content for unconditioned samples.

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