Time and Temperature Dependence of the Structural Evolution for Polyamide 1012

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Abstract The rheological property evolution of polyamide 1012 (PA1012) in the isothermal process in molten state has been investigated. The results show that the viscosity increases and crosslinking reaction occurs simultaneously together with the increase of temperature, thus causing the variation of storage modulus ($G'$) and loss modulus ($G''$) in the repeated frequency sweeps with residual time. This research has pointed out that the superposition is valid for monitoring the complex behavior composed of the viscosity increasing and crosslink occurring process by tracing the variation behavior of the crossover points of $G'$ and $G''$ with time, revealing the same time-temperature dependence of the two reactions in the isothermal process. A normalized master curve has been proposed to describe the melt behavior at a given temperature.

Keywords Polyamide 1012; Rheology; Crosslinking; Viscosity increasing; Time-temperature superposition

EXPERIMENTAL

Materials and Sample Preparation
PA1012 with melting temperature $T_m = 189 \, ^\circ C$ (Fig. S1, in the electronic supplementary information, ESI) was supplied by Shandong Guangyin New Materials Co., Ltd. It was synthesized from decamethylene diamine and dodecanedioic acid, which are produced by a microbiological fermentation method.\textsuperscript{[17]} The melt flow index of this material is 10.5 g/10min determined at 235 \, ^\circ C according to ASTM D1238 (2.16 kg). All the polyamide pellets were dried under vacuum at 100 \, ^\circ C for 12 h before the
experiments. The granule of the PA1012 was hot molded into plates with a diameter of 25 mm and thickness of 1 mm for the rheological tests.

**Rheological Experiments**

The rheological tests were carried out on a stress-controlled rotational rheometer (DHR-2, TA instrument) in a parallel plate geometry with a diameter of 25 mm and a gap size of 0.7 mm. All the experiments were performed in the linear viscoelastic regime under a nitrogen atmosphere. The rheological measurement was started at 180 s after the sample was placed in the apparatus. The repeated frequency sweep measurement was conducted at the given temperature $T$ with the frequency $\omega$ increasing from 500 rad/s to 0.1 rad/s without residual time between the sweeps. The steady-state flow test was conducted in the linear viscous regime at 220 °C with a strain of 5%. A fresh sample was applied for each test for consistency.

**Scanning Electron Microscopy (SEM)**

The samples that could not be dissolved in hexafluoro isopropanol (HFIP) formed gel-like transparent film. This film was freeze-dried in the freeze dryer (Shanghai EYELA Company) for 24 h. The micrographs from SEM were obtained with a JEOL JSM-6700F.

**RESULTS AND DISCUSSION**

**Structural Evolution of PA1012 in Rheological Tests**

Fig. 1(a) displays the representative curves in the repeated oscillatory sweep. The loss modulus $G''$ is higher than the storage modulus $G'$ in the investigated frequency range, revealing that viscous behavior is predominant at the beginning of the test. Meanwhile, $G'$ and $G''$ roughly obey the scaling law (slope of 1 and 2 for the plots of loss modulus $G''$ and storage modulus $G'$ against angular frequency $\omega$, respectively) in the terminal region, which is common in the rheologically simple systems. It is worthy to note that the modulus increases remarkably as the repeated sweeps continue, i.e. holding at the molten state, especially for the $G'$ value at low frequency with an increase of almost 2 orders ($10^2$ folds). The enhancement of modulus indicates the structural changes in the isothermal process. Besides, different from that in polymer nanocomposites where the deviation of $G'$ and $G''$ reflects the polymer viscoelasticity and the intrinsic elasticity of the fillers, that deviation responses to the “large” structural units merely, i.e. the entire polymer chain. The deviation of $G'$ and $G''$ from the scaling law in the viscoelastic flow zone means some structural change during holding in molten state and thus enhances the elasticity of the melt.

Moreover, there emerge two kinds of crossover points in

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**Fig. 1** (a) The storage $G'$ and loss modulus $G''$ as a function of angular frequency $\omega$ obtained from different sweep times at 220 °C, (b) the complex viscosity $\eta^*$ as a function of angular frequency $\omega$ with the raw data and the relevant fitting curves based on the Carreau-like equation, (c) the yield stress $\sigma_y$ as a function of residual time in the repeated frequency sweep, and (d) stress relaxation behavior for the samples with and without isothermal process.

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the later sweeps, which are indicative of two different transitions. As depicted by the red points and the dashed line drawn in Fig. 1(a), the crossover point in the high angular frequency region corresponds to the transition from the "solid-like" to "liquid-like" behavior (from $G^{'} > G^{''}$ to $G^{'} > G^{''}$), which represents the beginning of entire polymer chain relaxation. Its horizontal and vertical coordinates are marked as $\omega_0$ and $G_c$, respectively. As the residual time increases, the intersection moves to much lower frequency, which corresponds to larger timescale of chain relaxation. Considering the possible post-condensation reaction which made the viscosity increase between the end carboxyl and amine groups, the emergence and shift of this intersection is related with the increase of molecular weight due to this reaction. What is unusual is the appearance of another crossover point in the lower frequency range, beyond which $G^{'}$ prevails and thus, the system shows more elasticity. This crossover point probably originates from the formation of some three-dimensional network structure by crosslinking or gel formation when getting rid of any possible influence from fillers in the system. Herein, the point was denoted as $\omega_{cg}$ and $G_{cg}$. There exists much information in the shifts of the crossover points, and it will be discussed later in detail.

$$[\eta^* (\omega)] = \frac{\eta^*_0}{[1 + \lambda \omega]^n} + \frac{\sigma_0}{\omega} \quad (1)$$

Fig. 1(b) is the plot of complex viscosity $\eta^*$ as a function of angular frequency $\omega$ at different sweep time. It can be seen that there nearly exists a Newtonian plateau for the sample at the first sweep. As the sweep time increases, the viscosity is enhanced, especially at low angular frequency, and the shear-thinning becomes more prominent. When the oscillational sweeps continue, the shear-thinning behavior emerges throughout the whole frequency range. A simple Carreau-like equation (Eq. 1)[14] corrected by a yield stress is applied to study the rheological properties in detail. In this equation, $\eta^*_0$ is the zero-frequency complex viscosity; $\sigma_0$ represents the maximum shear stress where polymer can sustain before beginning to flow; $\lambda$ is the main relaxation time of the polymer; $n$ represents the flow index that quantifies the non-Newtonian feature of the polymer.[14] The fitting results are shown in Fig. 1(b), in which a good fitting correlation coefficient above 0.999 is obtained for all the fitting curves. The obtained parameters ($\eta^*_0$, $\lambda$, $n$) are shown in Fig. S1 (in ESI). The increase of $\eta^*_0$ can stem from the increase of the entanglement amount caused by crosslinking or molecular weight increases induced by post-condensation in the molten state.

As the condition of yield stress $\sigma_0 > 0$ has been regarded as the existence of a significant density of cross-links that hinder macroscopic flows,[14] $\sigma_0$ obtained from the fitting results with the Carreau-like equation is shown in Fig. 1(c). $\sigma_0$ grows in an exponential-like manner, indicating the formation of crosslinking network, which begins after an induction time,[14,21] and the enhancement of crosslink density in the thermal environment.[13,22] What needs stating is that the viscosity at low shear rate would become infinity due to the presence of yield stress. The finite viscosity value in the measurements, however, is ascribed to the finite testing time under a specific shear rate. Thus, the increase of $\eta^*_0$ mentioned before is contributed from both the viscosity increasing and the crosslinking structure formation.

To verify the speculation of crosslinking network, the solubility tests in hexafluoroisopropanol (HFIP) have been performed. There exist insoluble substances in the samples after the isothermal process. Detailed information on the solubility experiments shown in Table S1 (in ESI) reveals that the insoluble crosslinking content can reach approximately 93.9 wt% . Besides, formation of crosslinking network prevents chains from folding into lamellas and thus decreases crystallinity (Fig. S2 and Table S2 in ESI). The storage modulus $E'$ and glass transition temperature $T_g$ are also increased (Fig. S3 in ESI) as a result of the chain mobility reduction caused by the crosslinking network. This indicates that the mechanical property of polyamide can be improved by crosslinking, which is useful for polymer modification. Note that the molecular weight $M_w$, determined by derivative size exclusion chromatography (SEC) tests,[23] shows no evident difference between the samples with and without crosslinking, because the analyses only concern the fraction of fully reactive polyamide actually dissolved in the solvent.

In order to make the influence of thermal field on the polymer structure much clearer, the stress relaxation experiments have been performed for the samples with and without isothermal treatment in melt. The double-logarithm plot of the resultant data against time is shown in Fig. 1(d). There is one kind of relaxation behavior at long time that originates from the multi-scale relaxations of the polymer chain entanglements for the sample without the isothermal process in molten state. In contrast, for the sample after the isothermal treatment, there yields a crosslink-like plateau in the medium time scale followed by a rapid exponential decay in the longer time. It is clear that the motion of polymer chains is restricted by crosslinking architecture. Meanwhile, the crosslink is not stable under the shear field and cannot be sustained to a considerably long time. It is unusual because the permanently crosslinked polymers will not relax. The decline of the stress may result from the hydrolysis reactions promoted by water produced during the former post-condensation[14] and/or the thermal degradation. The main relaxation time $\lambda$ (Fig. S1b in ESI) increases to a maximum value followed by a slight decrease at about $2 \times 10^4$ s. The time value is close to that of the beginning of stress relaxation modulus $G(t)$ reduction for the crosslinked polymer in Fig. 1(d). So, the hydrolysis reactions and/or thermal degradation may be reasonable. Besides, flow sweeps were performed on these specimens (Fig. S4 in ESI). The sample after the isothermal process displays much higher plateau at low shear rates, accompanied with an additional shear thinning region aside from the region corresponding to chain slip that exists in the sample without isothermal process. This test has been performed several times, and the reproducible results are displayed. The higher plateau indicates the increase of molecular weight or and presence of crosslinking. The additional shear thinning region of the sample with isothermal treatment corresponds to the destruction of the long-range crosslinking structure. Both stress relaxation and steady shear flow indicate the existence of the crosslinking architecture and its influence on the rheological property.

Results based on the repeated frequency sweep have been...
analysed in depth to get a better understanding of the structural evolution in melt. Figs. 2(a) and 2(b) display the alteration of crossover frequency $\omega_c$ and modulus $G_t$ with the residence time at different temperatures, respectively. It shows that as the sweep time increases, the crossover point emerges in the low frequency region and shifts to higher frequency afterwards, which means that the crosslinking density increases and the average distance between the crosslinking points decreases. Meanwhile, the crossover points stemming from the disentanglement of the whole chain emerge and move to lower frequency as the isothermal process continues, revealing that the molecular weight increases when holding at elevated temperatures. The alterations of the crossover points indicate that the viscosity increasing and the crosslinking reaction occur simultaneously in the melt. The intersection emerges earlier with the increase of experimental temperature. Furthermore, the $\omega_c$-$t$ and $G_t$-$t$ plots obtained from different temperatures show similar trends. When getting a glance at the curves in Figs. 2(a) and 2(b), one can intuitively think of the superposition of intersection at different temperatures. There exists a critical crossover point in each temperature, which means the coincidence for the large portion chain disentanglement and the crosslinking transition. Calculating the first derivatives of the data curve $t$-$\omega_c$ and $t$-$G_t$ based on Figs. 2(a) and 2(b), respectively, and figuring out the point that its derivative was equal to zero, the critical values of $\omega_c$ and $G_t$ were obtained at each temperature. Thus, the location of the critical point in Fig. 2(c) was determined. $\omega_c$ and $G_t$ correspond to the location of the crossover point in the repeated frequency sweeps. Plotting $G_t$ as a function of $\omega_c$ to obtain the $G_t$-$\omega_c$ curve (Fig. 2c), the crossover point marked with filled symbol corresponds to the polymer entanglement relaxation, while the crossover point with open symbol means the formation of crosslinking. The $G_t$-$\omega_c$ curves composed of the two kinds of crossover points indicate the kinetics of the entanglement relaxation and crosslinking with time in different temperatures. The former critical point indicates the occurrence of crosslinking reaction and chain length increase caused by post-condensation at the same time. The critical points in the curves have been utilized to perform the superposition, or the normalization actually.

The coordinate value of the points in Fig. 2(c) is divided by that of the corresponding critical points at the same temperature to obtain the normalized curve shown in Fig. 2(d). Hence, the critical point will locate in the coordinate of 1 after the normalization. As shown in Fig. 2(d), the curves after normalization demonstrate good superposition. The scope of the curves extends to higher and lower normalized frequency by the contributions from the data of lower and higher temperatures, respectively. Fig. 2(d) can be divided into two distinct

Fig. 2 The crossover (a) frequency $\omega_c$ and (b) modulus $G_t$ as a function of residence time $t$ in the repeatant frequency sweep at different temperatures, and (c) the resultant $G_t$ change with $\omega_c$ and (d) the corresponding superposition curves. $G_t$ and $\omega_c$ in the inserted graph in (d) represent the transition values corresponding to that in (a) and (b), respectively.
regions by their locations and the slopes: the lower region corresponding to the formation of crosslinking architecture with a slope ranging from 0.81 to 0.87, and the upper region associated with the viscosity increasing reaction possessing a slope lower than 0.5. The slope of 0.5 is a meaningful value for the double-log $G$-$\omega$ graph in the rheological experiments, which is associated with the transition between elastic and viscous behavior. That is to say, the lower region of Fig. 2(d) implies the sample prominent in elasticity while the higher part mainly indicates viscosity, which is reasonable from the above-mentioned reactions.

The inserted graph in the lower right of Fig. 2(d) shows the $\omega_c$ and $G_c$ value of the critical point at each temperature, giving an intuitive impression about the horizontal and vertical shift amount of the data points in Fig. 2(c). Although there are no accurate horizontal and vertical shift factors ($a_t$, $b_t$) for the superposed procedure to obtain the activated energy, the data in the inserted plot show a clear linear relationship with temperature both for the $\omega_c$ and $G_c$ values. The linear relationship and final good superposition curves indicate that the two major reactions of post-condensation and crosslinking have the same time and temperature dependency although differing in reaction mechanisms. This means that increasing temperature has the same effect on the two reactions. What is more, the two reactions will increase the molecular weight and the melt viscosity, thus enhancing the melt strength, which will be of benefit to the foaming process.

**Morphology of the Crosslinking Sample**

The morphology of the insoluble floccus-like mass after freeze-drying is shown in Fig. 3. The void with the size smaller than 8 $\mu$m is the soluble part of the sample etched by HFIP. As vividly depicted in the pictures, the insoluble mass after the freeze-drying looks porous. It reveals that the crosslinking network exists in PA1012 after isothermal in melt.

![Fig. 3 The SEM image of the insoluble mass of PA1012 after freeze-drying.](image)

The PA1012 sample, prepared through polycondensation, will undergo viscosity increasing process because of further condensation reaction between the terminal carboxyl and amine groups. The FTIR experimental results (Fig. S5 and Table S3 in ESI) in our investigation on the structure of the samples with and without crosslinking show that the difference between them mainly lies in the relevant architecture about amide groups. This means that the amide groups are directly involved in crosslinking reactions, like that in the post-condensation induced viscosity increasing. Hence, the same time-temperature dependence of the two reactions originates from the same end groups diffusion control.

**CONCLUSIONS**

In this work, the repeated frequency sweep has been performed to monitor the structural evolution of PA1012 in the isothermal process in molten state. It has been found that PA1012 will undergo viscosity increasing and crosslinking process simultaneously, leading to the increase of $G''$ and $G'$. Moreover, the resultant crossover points, corresponding to the two reactions continuing those referred above, will converge to each other in the frequency sweep data curves. The most important observation in this research is that the superposition phenomenon for the crossover points represent the viscosity increasing and crosslinking, indicating the same time-temperature dependence for the two simultaneous reactions. This means that increasing temperature at the limited range can have the same effect on the molecular chain growth by further condensation and molecular chain crosslinking, all of which could increase the viscosity of the material. Besides, the two reactions will increase the molecular weight and viscosity of the melt, thus enhancing the melt strength and benefiting many subsequent applications, especially for the foaming process, etc.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2434-6.

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