

Time and Temperature Dependence of the Structural Evolution for Polyamide 1012

Liu Xin-Ran, Wang Yu, Liu Li-Yuan, Dong Xia, Wang Du-Jin

Cite this article as:

Liu Xin-Ran, Wang Yu, Liu Li-Yuan, Dong Xia, Wang Du-Jin. Time and Temperature Dependence of the Structural Evolution for Polyamide 1012[J]. *Chinese J. Polym. Sci.*, 2020, 38(9): 993-998. doi: 10.1007/s10118-020-2434-6

View online: <https://doi.org/10.1007/s10118-020-2434-6>

Articles you may be interested in

[Studies on Crystal Transition of Polyamide 11 Nanocomposites by Variable-temperature X-Ray Diffraction](#)

Chinese J. Polym. Sci. 2014, 32(1): 115 <https://doi.org/10.1007/s10118-014-1383-3>

[THERMO-CHEMICAL REACTIONS AND STRUCTURAL EVOLUTION OF ACRYLAMIDE-MODIFIED POLYACRYLONITRILE](#)

Chinese J. Polym. Sci. 2010, 28(3): 367 <https://doi.org/10.1007/s10118-010-9026-9>

[STRUCTURAL EVOLUTION AND COMPOSITION CHANGE IN THE SURFACE REGION OF POLYPROPYLENE/CLAY NANOCOMPOSITES ANNEALED AT HIGH TEMPERATURES](#)

Chinese J. Polym. Sci. 2009, 27(6): 879

[PMMA/PVDF共混体系相分离的时温依赖性](#)

TIME AND TEMPERATURE DEPENDENCE OF PHASE-SEPARATION BEHAVIOR FOR POLY(N-METHYL METHACRYLAMIDE)/POLY(VINYLIDENE FLUORIDE) BLENDS

高分子学报. 2009(2): 123 <https://doi.org/10.3724/SP.J.1105.2009.00123>

[不同热塑性树脂改性热固性树脂体系反应诱导相分离过程的时间/温度依赖性](#)

THE TIME/TEMPERATURE RELATIONSHIP DURING PHASE SEPARATION OF DIFFERENT THERMOPLASTIC MODIFIED THERMOSETTING SYSTEMS

高分子学报. 2007(8): 725

[一些热塑改性热固性树脂体系结构对反应诱导相分离时间/温度依赖性的影响](#)

THE EFFECT OF CHEMICAL STRUCTURE ON THE PHASE SEPARATION TIME/TEMPERATURE DEPENDENCIES IN SOME THERMOPLASTICS MODIFIED THERMOSET SYSTEMS

高分子学报. 2008(6): 600 <https://doi.org/10.3724/SP.J.1105.2008.00600>

Time and Temperature Dependence of the Structural Evolution for Polyamide 1012

Xin-Ran Liu^{a,b}, Yu Wang^{a,c}, Li-Yuan Liu^{a,b}, Xia Dong^{a,b*}, and Du-Jin Wang^{a,b}

^a CAS Key Laboratory of Engineering Plastics, CAS Research/Education Center for Excellence in Molecular Sciences, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

Electronic Supplementary Information

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

Citation: Liu, X. R.; Wang, Y.; Liu, L. Y.; Dong, X.; Wang, D. J. Time and temperature dependence of the structural evolution for polyamide 1012. *Chinese J. Polym. Sci.* 2020, 38, 993–998.

INTRODUCTION

Polymer processing,^[1–3] such as melting spinning,^[4] injection modelling,^[5,6] extrusion,^[7,8] and 3D printing,^[9,10] is usually performed above the melting temperature. Understanding the influence of processing procedure on the property of polymer melt is essential for the high-performance products. When subjected to elevated temperatures, the structure of polymer chains alters inevitably, and these reactions are more likely to occur compared with that in room temperature,^[11,12] especially for polymers with polar groups, e.g. amide, ester,^[13] and ether. As one of the excellent engineering plastics, polyamide is not intrinsically stable in the presence of oxygen and/or humidity, especially at high temperatures. The viscosity increasing, crosslinking, chain scission, and degradation are prone to happening for the molten polyamide.^[14,15] The change of the polymer structure will impact the processing and the final product quality,^[16] so it is vital to investigate the structural evolution of polymer under a thermal field. As a new kind of long aliphatic chain polyamide, polyamide 1012 (PA1012) possesses many advantages such as low water absorption, dimensional stability, superb toughness, and solvent resistance.^[17,18] Since PA1012 has become a commercial product just

for several years, researches on the relationship between its structure and property are sparse, especially on the structural evolution in the molten state. Rheometer is a sensitive tool for monitoring the structural change with small amplitude oscillatory sweep (SAOS) in the linear viscoelastic analysis, as it does not change the molecular structure during the test.^[15,19] Moreover, the frequency sweep can provide information on the polymer structure and the evolution dynamics over wide time scales. Especially, the low-frequency region is associated with the reptation mode of polymer chains, which implies the motion of the chain as a whole. In this research, rheological technique has been applied to investigate the structural transformation of PA1012 in the molten state. The repeated frequency sweep was utilized to monitor the viscoelastic response in the long-time regime.

EXPERIMENTAL

Materials and Sample Preparation

PA1012 with melting temperature $T_m = 189$ °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.^[17] The melt flow index of this material is 10.5 g/10min determined at 235 °C according to ASTM D1238 (2.16 kg). All the polyamide pellets were dried under vacuum at 100 °C for 12 h before the

* Corresponding author, E-mail: xiadong@iccas.ac.cn

Received February 9, 2020; Accepted March 24, 2020; Published online June 9, 2020

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 ω decreasing from 500 rad/s to 0.1 rad/s without residual time between the sweeps. The steady-state flow test was performed at 220 °C with the shear rate from 0.02 s⁻¹ to 200 s⁻¹. Stress relaxation experiment 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 ω , respectively) in the terminal region, which is common in the rheologically simple systems.^[20] 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 (10² 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

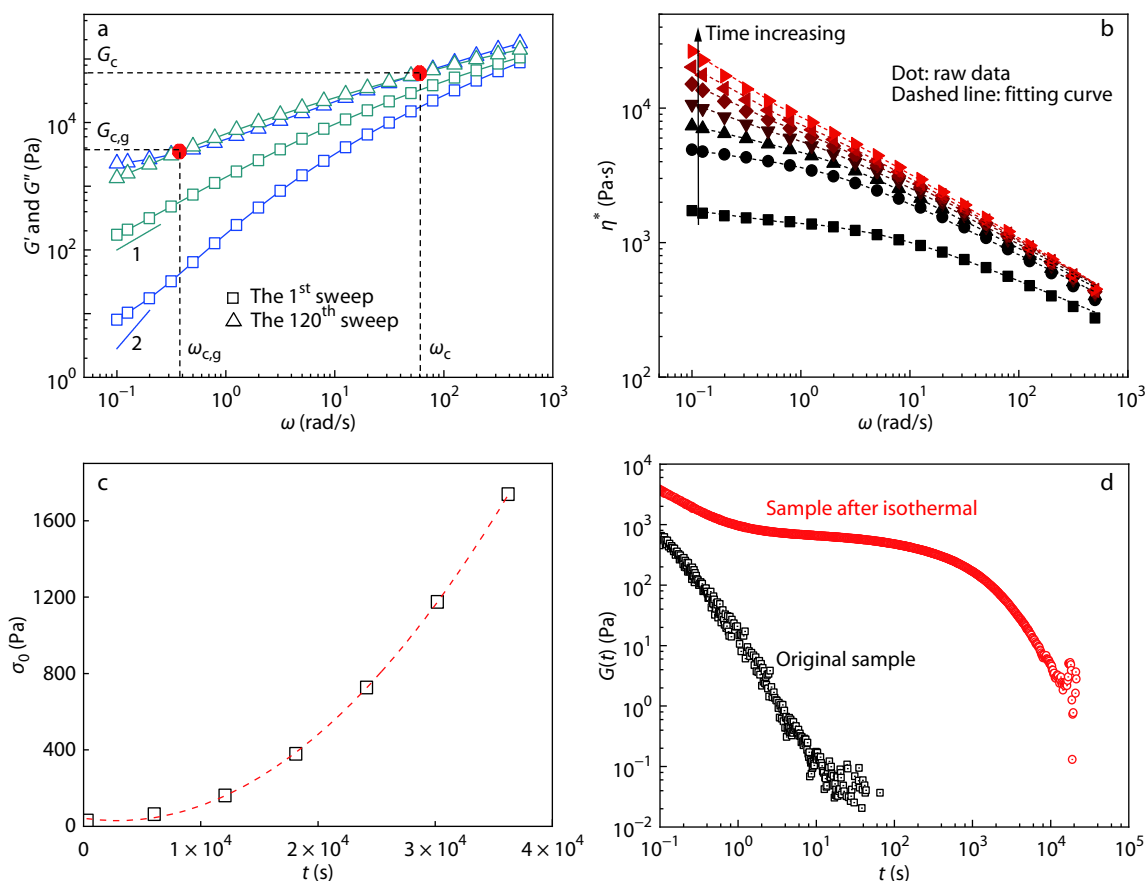


Fig. 1 (a) The storage G' and loss modulus G'' as a function of angular frequency ω obtained from different sweep times at 220 °C, (b) the complex viscosity η^* as a function of angular frequency ω with the raw data and the relevant fitting curves based on the Carreau-like equation, (c) the yield stress σ_0 as a function of residual time in the repeated frequency sweep, and (d) stress relaxation behavior for the samples with and without isothermal process.

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 ω_c 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,^[13] 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 $\omega_{c,g}$ and $G_{c,g}$. There exists much information in the shifts of the crossover points, and it will be discussed later in detail.

$$|\eta^*(\omega)| = \frac{\eta_0^*}{[1 + \lambda\omega]^{1-n}} + \frac{\sigma_0}{\omega} \quad (1)$$

Fig. 1(b) is the plot of complex viscosity η^* as a function of angular frequency ω 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, η_0^* is the zero-frequency complex viscosity; σ_0 represents the maximum shear stress where polymer can sustain before beginning to flow; λ 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 (η_0^* , λ , n) are shown in Fig. S1 (in ESI). The increase of η_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] σ_0 obtained from the fitting results with the Carreau-like equation is shown in Fig. 1(c). σ_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 η_0^* mentioned before is contributed from both the viscosity increasing and the crosslink-

ing 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 λ (Fig. S1b in ESI) increases to a maximum value followed by a slight decrease at about 2×10^4 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 ω_c and modulus G_c 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 ω_c - t and G_c - 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 - ω_c and t - G_c 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 ω_t and G_t were obtained at each temperature. Thus, the location of the critical point in Fig. 2(c) was determined. ω_c and G_c correspond to the location of the crossover point in the repeated frequency sweeps. Plotting G_c as a function of ω_c to obtain the G_c - ω_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_c - ω_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

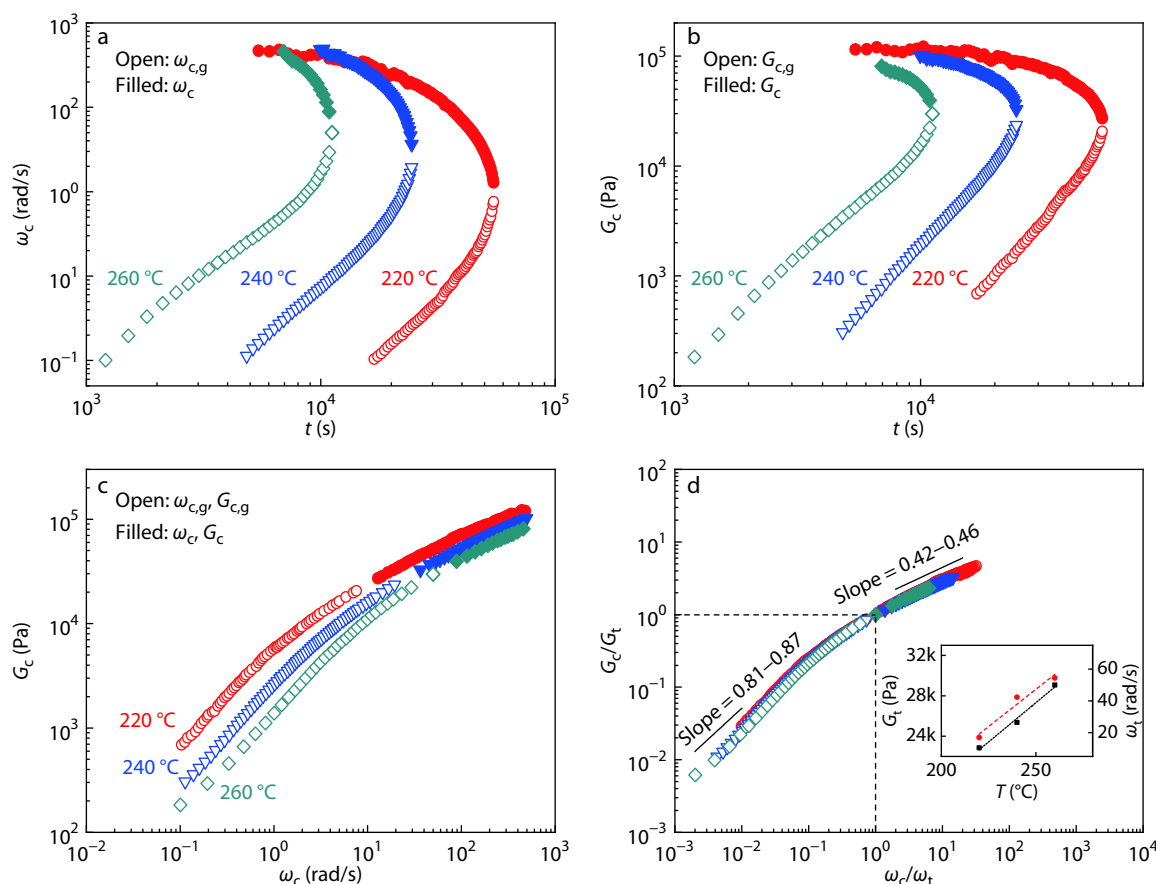


Fig. 2 The crossover (a) frequency ω_c and (b) modulus G_c as a function of residence time t in the repeatant frequency sweep at different temperatures, and (c) the resultant G_c change with ω_c and (d) the corresponding superposition curves. G_t and ω_t in the inserted graph in (d) represent the transition 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,^[24] 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 ω_c and G_c value of the critical point at each temperature, giving an intuitional 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 ω_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 μm 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.

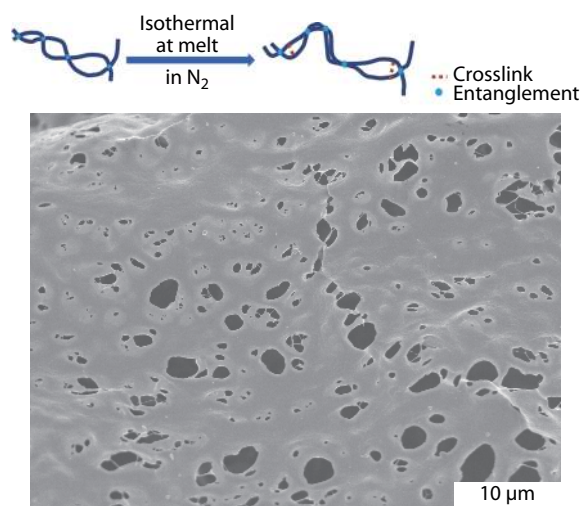


Fig. 3 The SEM image of the insoluble mass of PA1012 after freeze-drying.

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 Ta-

ble 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 cross-linking reactions,^[14] 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>.

ACKNOWLEDGMENTS

This work was financially supported by the National Key R&D Program of China (No. 2017YFB0307600) and the National Natural Science Foundation of China (No. 21574140).

REFERENCES

- 1 Wilzer, J.; Windmann, M.; Weber, S.; Hill, H.; Bennekorn, A. V.; Theisen, W. Thermal conductivity of advanced TiC reinforced metal matrix composites for polymer processing applications. *J. Compos. Mater.* **2015**, 49, 243–250.
- 2 Schaller, R.; Neerincx, P. E.; Meijer, H. E. H. Hierarchical and fractal structuring in polymer processing. *Macromol. Mater. Eng.* **2017**, 302, 1600524.
- 3 Al-Mezrakchi, R. Y. H. An investigation into scalability production of ultra-fine nanofiber using electrospinning systems. *Fibers Polym.* **2018**, 19, 105–115.
- 4 Karbownik, I.; Rac, O.; Fiedot, M.; Suchorska-Woźniak, P.; Teterycz, H. *In situ* preparation of silver-polyacrylonitrile nanocomposite fibres. *Eur. Polym. J.* **2015**, 69, 385–395.
- 5 Yang, Y.; Yang, B.; Zhu, S.; Chen, X. Online quality optimization of the injection molding process via digital image processing and

- model-free optimization. *J. Mater. Process. Technol.* **2015**, 226, 85–98.
- 6 La, R.; Zhou, Q.; Xia, C.; Mi, D.; Zhang, J. The banded spherulites of iPP induced by pressure vibration injection molding. *Chinese J. Polym. Sci.* **2015**, 33, 1625–1632.
 - 7 Schäfer, C.; Meyer, S. P.; Osswald, T. A. A novel extrusion process for the production of polymer micropellets. *Polym. Eng. Sci.* **2018**, 58, 2264–2275.
 - 8 Huang, Z.; Luo, P.; Tong, J.; Su, F. Velocity distribution of extensional flow fields in an eccentric cylinder of an extensional extruder. *J. Macromol. Sci., Part B: Phys.* **2018**, 57, 732–745.
 - 9 Ji, Z.; Zhang, X.; Yan, C.; Jia, X.; Xia, Y.; Wang, X.; Zhou, F. 3D printing of photocuring elastomers with excellent mechanical strength and resilience. *Macromol. Rapid Commun.* **2019**, 40, 1800873.
 - 10 Li, X.; Yu, R.; He, Y.; Zhang, Y.; Yang, X.; Zhao, X.; Huang, W. Self-healing polyurethane elastomers based on a disulfide bond by digital light processing 3D printing. *ACS Macro Lett.* **2019**, 8, 1511–1516.
 - 11 Shangguan, Y.; Zhang, C.; Xie, Y.; Chen, R.; Jin, L.; Zheng, Q. Study on degradation and crosslinking of impact polypropylene copolymer by dynamic rheological measurement. *Polymer* **2010**, 51, 500–506.
 - 12 Cuadri, A. A.; Martín-Alfonso, J. E. The effect of thermal and thermo-oxidative degradation conditions on rheological, chemical and thermal properties of HDPE. *Polym. Degrad. Stab.* **2017**, 141, 11–18.
 - 13 Kruse, M.; Wagner, M. H. Time-resolved rheometry of poly(ethylene terephthalate) during thermal and thermo-oxidative degradation. *Rheol. Acta* **2016**, 55, 789–800.
 - 14 Filippone, G.; Carroccio, S. C.; Mendichi, R.; Gioiella, L.; Dintcheva, N. T.; Gambarotti, C. Time-resolved rheology as a tool to monitor the progress of polymer degradation in the melt state. Part I: thermal and thermo-oxidative degradation of polyamide 11. *Polymer* **2015**, 72, 134–141.
 - 15 Salehiyan, R.; Bandyopadhyay, J.; Ray, S. Mechanism of thermal degradation-induced gel formation in polyamide 6/ethylene vinyl alcohol blend nanocomposites studied by time-resolved rheology and hyphenated thermogravimetric analyzer Fourier transform infrared spectroscopy mass spectroscopy: synergistic role of nanoparticles and maleic anhydride-grafted polypropylene. *ACS Omega* **2019**, 4, 9569–9582.
 - 16 Dong, S.; Zhu, P.; Liu, J.; Wang, D.; Dong, X. Thermal treatment effects on the microstructure and tensile properties of transparent polyamides. *Acta Polymerica Sinica* (in Chinese) **2019**, 50, 189–198.
 - 17 Wang, L.; Dong, X.; Huang, M.; Müller, A. J.; Wang, D. Self-associated polyamide alloys with tailored polymorphism transition and lamellar thickening for advanced mechanical application. *ACS Appl. Mater. Interfaces* **2017**, 9, 19238–19247.
 - 18 Gao, Y.; Dong, X.; Wang, L.; Liu, G.; Liu, X.; Tuinea-Bobe, C.; Whiteside, B.; Coates, P.; Wang, D.; Han, C. C. Flow-induced crystallization of long chain aliphatic polyamides under a complex flow field: inverted anisotropic structure and formation mechanism. *Polymer* **2015**, 73, 91–101.
 - 19 Suchocki, C.; Molak, R. Rheological properties of polyamide: experimental studies and constitutive modeling. *Chinese J. Polym. Sci.* **2019**, 37, 178–188.
 - 20 Hoffmann, B.; Kressler, J.; Stöppelmann, G.; Friedrich, C.; Kim, G.-M. Rheology of nanocomposites based on layered silicates and polyamide-12. *Colloid. Polym. Sci.* **2000**, 278, 629–636.
 - 21 Okamba-Diogo, O.; Richaud, E.; Verdu, J.; Fernagut, F.; Guilment, J.; Fayolle, B. Molecular and macromolecular structure changes in polyamide 11 during thermal oxidation. *Polym. Degrad. Stab.* **2014**, 108, 123–132.
 - 22 Chen, Y.; Wei, W.; Himmel, T.; Wagner, M. H. Structure and rheological behavior of thermoreversible supramolecular polymers with weak multiple hydrogen bonds. *Macromol. Mater. Eng.* **2013**, 298, 876–887.
 - 23 Schuttenberg, H.; Schulz, R. C. Trifluoroacetylation of amines with N-trifluoroacetyl-nylon 66. *Angew. Chem. Int. Ed.* **1976**, 15, 777–778.
 - 24 Ibar, J. P.; Zhang, Z.; Li, Z. M.; Santamaria, A. Investigation of the dynamic rheological properties of a polycarbonate melt presenting solid-like characteristics and a departure from pure liquid newtonian behavior at long relaxation times. *J. Macromol. Sci., Part B: Phys.* **2015**, 54, 649–710.