**Influence of Annealing on the Mechanical α_c -relaxation of Isotactic Polypropylene: A Study
from the Intermediate Phase Perspective**

Baobao Chang^{a,b}, Konrad Schneider^{a*}, Roland Vogel^a, Gert Heinrich^a

- a. Leibniz-Institut für Polymerforschung Dresden, Germany
- b. Institut für Werkstoffwissenschaft, Technische Universität Dresden, Germany

Mr. Baobao Chang: chang@ipfdd.de

Dr. Roland Vogel: vogel@ipfdd.de

Prof. Dr. Gert Heinrich: gheinrich@ipfdd.de

*Corresponding author: Dr. Konrad Schneider

Telephone: +49 351 4658 360

Fax: +49 351 4658 362

Email: schneider@ipfdd.de

Abstract

In this work, the influence of annealing on the mechanical α_c -relaxation behavior of isotactic polypropylene (iPP) was investigated by small angle X-ray scattering (SAXS), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). The results suggest that the annealing induced imperfect lamellae melting and secondary crystallization greatly influences the mechanical α_c -relaxation. In the sample quenched to 10 °C, crystallites with a broad size distribution are formed. The polymer chains in the intermediate phase are constrained by the crystallite, leading to one broad α_c -relaxation peak with an activation energy of 53.39 kJ/mol. Annealing at 45 °C reduces the activation energy to 42.19 kJ/mol which is a result of the rearrangement of polymer chains in the intermediate phase. With an annealing temperature between 60 °C-105 °C imperfect lamellae melting releases part of the constraining force, which reduces the conformational ordering of the polymer chains near the amorphous phase. Consequently, two separate α_c -relaxation peaks could be observed which are labeled as α_{c1} -relaxation and α_{c2} -relaxation in the order of increasing temperature. α_{c1} -relaxation and α_{c2} -relaxation describe the relaxation behavior of polymer chains in the region close to the amorphous phase and the crystalline phase, respectively. Both relaxation peaks shift to a higher temperature as annealing temperature increases. In this range, the activation energy of α_{c1} -relaxation decreases drastically from 38.43 kJ/mol to 35.55 kJ/mol as the thickness of the intermediate phase increases from 2.1 nm to 2.15 nm. With an annealing temperature higher than 105 °C, a new crystalline phase is formed in the intermediate phase, which enhances the constraining force on the polymer chains. As a result, the α_{c1} -relaxation peak is broadened and its position shifts to a higher temperature as the annealing temperature increases. Moreover, the polymer chains in the region between the initial crystalline phase and the newly formed crystalline phase are strongly confined. Therefore, the α_{c2} -relaxation is undetectable. The activation energy of α_{c1} -relaxation decreases from 23.58 kJ/mol to 13.68 kJ/mol as the intermediate phase increases from 2.26 nm to 2.99 nm.

Keywords: mechanical α_c -relaxation, intermediate phase, isotactic polypropylene

1. Introduction

Isotactic polypropylene (iPP) is one of the most versatile thermoplastic polymer used in a wide variety of applications including cables, packaging, and automotive components, due to its outstanding properties, such as low dielectric loss, good heat resistance, non-toxicity and good mechanical properties.¹⁻³ The relationship between mechanical properties and microstructure of iPP has long been a hot topic since it was polymerized by G. Natta in 1954.⁴ In the past few years, the mechanical relaxation behavior of iPP has been investigated by plentiful studies. Generally, iPP displays four relaxation peaks in the plot of loss angle ($\tan\delta$) as a function of temperature. The peaks are designated as δ , γ , β , and α_c -relaxation, in the order of increasing temperature.⁵⁻¹⁵ δ -relaxation, located mainly below 100 K, is related to the hindered rotation of CH_3 groups.¹⁶ γ -relaxation appeared between 150 K and 230 K, is attributed to the local motions of chain ends or branches in the amorphous phase.¹² β -relaxation (the glass-rubber transition) situated between 250 K and 300 K is attributed to cooperative motions of chain segments in the amorphous phase.^{11,17-20} α_c -relaxation is localized below the melting temperature. Although abundant studies have been performed, the genesis of α_c -relaxation is still uncertain and sometimes even controversial in the literatures.^{6,7,9,11,15,21} In some cases, the multiple nature of α_c -relaxation even complicates the situation.^{9,21} Normally, α_c -relaxation exists only in the presence of the crystalline phase. Hence, the simplest hypothesis is to assign it to some phenomenon occurring in the crystalline phase. McCrum¹⁵ pointed out that its origin is most likely an additional relaxation of the amorphous fraction triggered by the onset of molecular rotation within the crystal. Jourdan¹¹ suggested that α_c -relaxation originating within the crystalline phase could be attributed to the long-distance stress-assisted diffusion of defects inside the crystalline phase. But the amorphous phase also played an important role, because defects have to adapt themselves to the deformation compatibility of crystalline and amorphous phases by cooperative movements. Pluta⁹ proposed that in the case of samples containing large spherulites, the α_c -relaxation could be attributed to the friction phenomena between boundaries of the crystalline lamellae and to a certain contribution arising from the intralamellar regions accompanied by restricted reorientation of crystalline elements within oriented lamellae. For nonspherulitic samples, two components of the α_c -relaxation process were found. The low-temperature component was attributed to the stress relaxation of the fraction of the noncrystalline phase containing strained molecules and segments of molecules belonging to the specific (irregular) arrangement of the surface layer of the crystallites. The high-temperature component was connected with the viscous slip process of the crystalline elements within the noncrystalline phase. Moreover, the high-temperature component of the α_c -relaxation process could be strongly affected by orientation²¹ or the length of chain folding at the interphase between a crystalline phase and an amorphous phase.¹⁵ In the reviews by Boyd,^{6,7} a viewpoint was proposed that the two-phase model of well-developed crystals plus the amorphous phase may be inadequate to illustrate the origin of α_c -relaxation, and, as consequence, an additional intermediate phase should be taken into

consideration. This proposal was further demonstrated in the work by Hu with the help of nuclear magnetic resonance spectroscopy: the chain diffusion occurring at the intermediate phase is responsible for α_c -relaxation.^{22,23}

The position and intensity of α_c -relaxation vary with many factors (thermal history, crystalline structure, density, etc.). To name a few, Tiemblo¹⁰ studied the relationship between α_c -relaxation and thermooxidation kinetics of PP. The results revealed that samples bearing α_c -relaxation show a strong decrease in p_0 at temperatures below 115 °C, where the parameter p_0 is related to the initial concentration of oxidizable sites. However, the decrease in p_0 is not observed in samples where the α_c -relaxation is not resolved. In their late work,^{13,24} the relative influence of microstructure, molar mass and morphology of PP on α_c -relaxation was assessed. Among the factors considered, microstructure and isotactic average length (n_1) have been found to drive mainly the quality of α_c -relaxation. The intensity of α_c -relaxation depends on the final crystalline distribution, provided the requirements that some microstructural features related to n_1 are fulfilled. On the other hand, a critical average isotactic length around 30 propylene units has been found, below which the β -relaxation are promoted with respect to the α_c -relaxation. The fraction of the low melting point crystals, which determines the degree of constraint within the interlamellar region, drives the relative intensities of α_c - and β -relaxation processes. In a recent work, Suljovrujic¹⁴ proved that the position, intensity and activation energy of α_c -relaxation were strongly affected by gamma radiation exposure. The intensity of α_c -relaxation increased nonlinearly with absorbed dose and the shift in the position of the α_c -relaxation is most intensive for iPP exposed to lower doses (≤ 100 kGy). In addition, the evolution of the activation energy with absorbed dose is relatively similar to that observed for the position of α_c -relaxation.

The scope of the present work focuses on the relationship between mechanical α_c -relaxation and the intermediate phase of iPP. As in the case of most of the semi-crystalline polymers,²⁵⁻²⁸ the formation of the intermediate phase in iPP could be greatly influenced by annealing.²⁹⁻³⁴ Therefore, samples with different well-defined thermal history were prepared by annealing the quenched iPP at different temperatures for a different time. For comparison, samples were also prepared by melt crystallization. With the analysis of the results of this study, we attempt to gain a further insight into the mechanical α_c -relaxation in semi-crystalline polymers.

2. Experimental section

2.1. Materials and sample preparation

A homo-iPP, grade HD120MO from Borealis (Linz, Austria), is used in this study. The melt flow index is 8 g/10 min under ASTM D1238 conditions of 230 °C and 2.16 kg. The weight-average and number-average molecular weight is 365 kg/mol and 67.6 kg/mol, respectively. The plates with a thickness of 1 mm were compression molded with a hot press (Vogt, Germany) in the following

procedure: firstly, the thermo-mechanical history of the plates was erased by keeping the plates at 210 °C for 10 min, afterwards the plates were quenched immediately into water (10 °C) or transferred to another hot press at a temperature of 90 °C, 100 °C, 105 °C, 110 °C, 115 °C, 120 °C, and 130 °C until the finish of the melt crystallization; and then, the quenched plates were annealed in a vacuum oven (Thermo Scientific, USA) with assigned temperature of 45 °C, 60 °C, 75 °C, 90 °C, 105 °C, 120 °C, 135 °C, and 150 °C for different time. The sample quenched to 10 °C was named as Q10, the samples prepared by melt crystallization as MT_c and the samples prepared by annealing as AT_a -t. For instance, M120 means that the plate was melt crystallized at 120 °C, and A75-2 means that the sample was prepared by annealing Q10 at 75 °C for 2 h.

2.2. Characterization

Small angle X-ray scattering (SAXS) measurement

SAXS measurements were performed at PETRA III at the Deutsches Elektronen-Synchrotron (DESY, Hamburg, Germany). The wavelength of the X-ray beam was calculated to be 1.06917 Å. SAXS patterns were recorded by a two-dimensional PILATUS 1M-detector (981×1043 pixels of 172×172 μm²). The sample-to-detector distance was 4961 mm. Background subtraction of the SAXS patterns was processed with PV-wave software. 1D-SAXS curves were obtained by a circular integration of the 2D patterns.

Differential scanning calorimetry (DSC) measurement

DSC measurements were performed on Q2000 (TA Instruments, USA). Dry nitrogen was used as a purge gas at a rate of 50 mL/min. A 5 mg sample sealed in an aluminum pan was heated from -80 °C to 200 °C with a heating rate of 10 °C min⁻¹. For temperature-modulated DSC (TMDSC) measurement, the parameters were as follows: the temperature amplitude is 0.318 K, the oscillation period is 40 s, and the heating rate is 2 °C/min.

Dynamic mechanical analysis (DMA)

The mechanical relaxation behavior was measured using an ARES G2 rheometer (TA Instruments, USA). The specimen (the width is 11 mm, the thickness is 1 mm and the free length is 10 mm) was cut from compression molded plate. All measurements were carried out using nitrogen as the heating gas. Each test was started 4 min after insertion the specimen into the rheometer, to allow the attainment of thermal equilibrium. The testing frequency was 1 rad/s, the strain was 0.05 %, the heating rate was 5 °C/min and the temperature range was -70 °C to 160 °C. For the temperature-frequency sweep tests, the specimens were scanned from 0.05 rad/s to 100 rad/s at different temperatures (-70 °C to 160 °C in steps of 5 °C).

3. Results and discussion

3.1. Microstructure of iPP with different thermal history

Fig. 1 shows the 1D-SAXS curve for iPP with various thermal histories. Lorentz correction ($I(q) \rightarrow q^2 I(q)$) is employed because that no lamellae orientation exists in the hot pressed samples.³⁵ $q=4\pi\sin\theta/\lambda$, λ is the X-ray wavelength, θ is the scattering angle. The long period (L_p), containing one crystalline phase, one amorphous phase, and one intermediate phase, could be estimated from the peak position (q_{max}) in 1D-SAXS curve, $L_p=2\pi/q_{max}$. In addition, the width of the scattering peak (full width at half maximum, $FWHM$) providing the information about the statistics of the long period could be obtained by peak fitting. In **Fig. 1a'**, one can see that with the increase of crystallization temperature, L_p of melt crystallized iPP increases linearly from 15.2 nm to 20.0 nm. And $FWHM$ decreases slightly from 0.19 nm⁻¹ to 0.15 nm⁻¹. For Q10, L_p is 11.0 nm and $FWHM$ is 0.30 nm⁻¹. Annealing at 45 °C for 6 h has a negligible effect on both L_p and $FWHM$. As annealing temperature further increases, L_p increases continually from 11.6 nm to 18.25 nm. And $FWHM$ decreases from 0.28 nm⁻¹ to 0.13 nm⁻¹. **Fig. 1c** provides the 1D-SAXS curve for the samples annealed at 75 °C for different times. A slight increase of L_p and decrease of $FWHM$ could be found after annealed for 1 h, and then both of them keep nearly constantly until 6 h. For the samples annealed at 135 °C (**Fig. 1d'**), the scenario is quite different. An obvious increase of L_p from 11.0 nm to 16.4 nm and decrease of $FWHM$ from 0.30 nm⁻¹ to 0.15 nm⁻¹ could be found in 2 h. After that, L_p and $FWHM$ have a little change.

Fig. 1 Lorentz-corrected 1D-SAXS curves on the left side, long period (L_p) and full width at half maximum of the scattering peak ($FWHM$) on the right side. Samples prepared by melt crystallization (a) and (a'); by annealing at different temperatures for 6 h (b) and (b'); by annealing at 75 °C for different times (c) and (c'); and by annealing at 135 °C for different times (d) and (d').

In **Fig. 1b** a shoulder peak at higher q value shows up for the sample annealed at a temperature higher than 105 °C. Generally, there are two possible origins for the appearance of the shoulder peak: secondary crystallization during annealing, resulting in the formation of new lamellae with larger L_p ; or the perfection of original lamellae, leading to a higher order scattering peak. In our case, the former one is preferred, which will also be verified in the following part by DSC and TMDSC. The shoulder peak in **Fig. 1d** can be ascribed to the same origin above mentioned.

The domain thickness, including the thickness of crystalline phase, the intermediate phase, and amorphous phase could be readily described by one-dimensional correlation function ($K(z)$) without resorting to any models.³⁵⁻⁴² The prerequisite for $K(z)$ is that the density in each phase should be different. In iPP, the density of the intermediate phase has been proved to be 10-15% lower than that of the crystalline phase, but higher than that of the amorphous phase.²⁵ Therefore, $K(z)$ is employed in this study and it is given as follows:

$$K(z) = \frac{\int_0^\infty q^2 I(q) \cos(qz) dq}{\int_0^\infty q^2 I(q) dq} \quad (1)$$

where z represents the length in real space with a unit of nm. **Fig. 2** gives a representative $K(z)$ curve of iPP. The thickness of the intermediate phase (L_{im}) and the amorphous phase (L_a) can be determined by the upper and lower limits of the straight line section. Then, the thickness of crystalline phase (L_c) can be acquired by subtracting $2L_{im}$ and L_a from L_p . The $K(z)$ curves for all the samples could be found in Figure S1 in the **Supporting Information**. The domain thickness of iPP with various thermal histories is summarized in **Fig. 3a**.

Fig. 2 A representative $K(z)$ curve of iPP as a function of z

In **Fig. 3a**, one can see that for the melt crystallized iPP, only a slight increase of L_a and L_{im} could be found as the crystallization increases. But, an evident increase can be found for L_c which satisfies Strobl' theory⁴³ that the reciprocal of L_c should be linearly related to the crystallization temperature. In the meantime, the ratio of L_{im}/L_c decreases as crystallization temperature increases, coinciding with the results from other literature.^{31,44} During melt crystallization, the mobility of polymer chains is quite high. The formation of perfect regular fold-surfaces crystalline phase is preferred and the coupling between the crystalline phase and the amorphous phase is weak.^{44,45} Consequently, the formation of the intermediate phase is restricted.

For Q10, the values of L_c , L_a and L_{im} are 3.83 nm, 3.75 nm, and 2.02 nm. The influence of annealing temperature on the domain thickness evolution after annealing could be divided into three regions (see **Fig. 3b**). Region I: with an annealing temperature lower than 45 °C, in this range weak influence can be found on the domain thickness; Region II: from 60 °C to 90 °C, in this range L_{im} and L_c keeps nearly constant, but L_a increases slightly; Region III: from 105 °C to 150 °C, all the domain thickness L_c , L_a , and L_{im} increase obviously with the increase of annealing temperature. L_c increases from 4.15 to 6.08 nm, L_a from 3.93 to 5.33 nm and L_{im} from 2.4 to 3.2 nm. The influence of the annealing time on the domain thickness evolution is given in **Fig. 3c** and **Fig. 3d**. One can see that L_c , L_a , and L_{im} of iPP

annealed at 75 °C for different times hardly change. Whereas, drastic increases of L_c and L_a could be found for iPP annealed at 135 °C for 2 h. L_c increases from 4.12 to 4.86 nm, L_a increases from 3.89 to 5.24 nm. After that, the slight increase can be found for L_c and L_a until 6 h. As to L_{im} , the evident increase from 2.02 to 2.33 nm could be found in 0.5 h, and then it grows gradually until 6 h.

Fig. 3 The crystalline phase thickness (L_c), the intermediate phase thickness (L_{im}) and the amorphous phase thickness (L_a) of iPP prepared by melt crystallization (a), annealing at different temperatures for 6 h (b), annealing at 75 °C for different times (c), and annealing at 135 °C for different times (d)

The evolution of domain thickness during isothermal annealing is an irreversible process. Sanchez⁴⁶ proposed that the rate of lamellae thickening is proportional to the derivative of the surface free energy with respect to lamellae thickness, which could be depicted by the following equation:⁴⁶

$$x^2 \frac{dl}{dt} = -k_0 \exp[-v\Delta H(T_m^0 - T)/RTT_m^0] \frac{dG_s}{dl} \quad (2)$$

where x and l are the lateral dimension and thickness of crystalline phase, G_s is the surface free energy, t is the annealing time, k_0 is a proportionality constant, ΔH is the heat of fusion per mole of molecular chains, T_m^0 is the equilibrium melting point, T is the annealing temperature, and v is the number of molecular chains which diffuse from amorphous phase to crystalline phase simultaneously. The surface free energy G_s of a lamellar crystal with square cross section is given by

$$G_s = 4xl\sigma + 2x^2\sigma_e = 4(lV)^{1/2}\sigma + 2V\sigma_e/l \quad (3)$$

where σ_e is the surface free energy of the basal plane, σ is the surface free energy of the lateral surface, and $V=x^2l$ is the volume of the crystalline phase. At a certain thickness l^* , $dG_s/dl=0$ and the crystal will reach its equilibrium dimensions of l^* and a corresponding x^* . It is easily shown that, if the volume V of crystal remains constant, then

$$l^* = (\sigma_e^2 V / \sigma^2)^{1/3} \quad (4)$$

$$x^* = (\sigma V / \sigma_e)^{1/3} \quad (5)$$

$$l^*/x^* = \sigma_e/\sigma \quad (6)$$

Therefore, for a single lamella, if l/x is smaller than l^*/x^* , the lamella can reduce its surface free energy by an increase in l and a decrease in x . But if the initial ratio of l/x exceeds l^*/x^* , the direction would be the melting of the lamella. Therefore, depending on the size of the initial crystalline phase two competitive processes could happen: one is the melting process if l/x exceeds l^*/x^* , the other one is the lamellae thickening process if l/x is smaller than l^*/x^* .

In region I, no structural change could be detected by SAXS. In region II, L_{im} and L_c keep constantly, $FWHM$ decreases drastically and L_a increases slightly. The results suggest that imperfect lamellae melting are the dominant process in this region. Lamellae thickening hardly happen because the mobility of polymer chains is too weak. In region II, the decrease of $FWHM$ continues and an evident increase of the L_c , L_a and L_{im} shows up, which means that in this region lamellae thickening and imperfect lamellae melting coexist. At higher annealing temperature, more lamellae melt providing more space and polymer chains for the lamellae thickening process. Besides, the polymer chains mobility enhances with the increase of annealing temperature. Annealing at 135 °C for different time provides more details about the process. The increase of the intermediate phase thickness finishes in 0.5 h, but the thickening of the crystalline phase and the melting of the imperfect lamellae sustain until 2 h. Generally, the lamellae thickening proceeds by transforming the intermediate phase into it which was verified by Lei and his coworkers.⁴⁰ In their work, in-situ small angle X-ray scattering is employed to detect the domain thickness evolution during annealing, and a slight decrease of the intermediate phase thickness at the beginning of annealing and the afterward increase has been observed. The reason responsible that can be given as follows: in semi-crystalline polymers, the polymer chains directly neighboring the crystalline phase have a higher conformational ordering compared to those away from the surface of the crystalline phase. Thus, a lower energy barrier is needed for the transformation from the intermediate phase to the crystalline phase.^{34,47}

3.2. Thermal stability of iPP with different thermal history

The thermal stability of iPP with different thermal history is provided in **Fig. 4**. Two melting peaks could be found for M90 in **Fig. 4a**. With the increase of melt crystallization temperature, the peak on left side shifts to a higher temperature gradually. And finally the double melting peaks merger into one for M130. The appearance of the double melting peaks is caused by the low cooling rate during melt crystallization. Primary crystallization starts before the melt reaching the preset temperature, giving rise to the melting peak on the right side. Secondary crystallization happens at the preset temperature resulting in the melting peak on the left side. With the increase of the melt crystallization temperature, primary crystallization is inhibited. The merging of the double melting suggests that the polydispersity of the crystalline phase thickness in melt crystallized is decreased, which coincides with the decrease of *FWHM* in the 1D-SAXS curve. For Q10, only one melting peak at 166 °C could be found in **Fig. 4b**. As annealing temperature increases, the peak position keeps constantly. For the samples annealed at a temperature higher than 105 °C, a shoulder peak (indicated by the arrows in **Fig. 4b**) could be found at the lower temperature side of the main peak. The shoulder peak becomes better distinguished and its position shifts gradually from 113 °C to 151 °C with the increases of annealing temperature. The appearance of the shoulder peak is assigned to the melting of newly formed crystallites formed after annealing,^{39,48} which confirms the result in 1D-SAXS that at high annealing temperature new crystalline phase are formed. **Fig. 4c** suggests that annealing at 75 °C has a negligible effect on the crystalline phase, as has been found in **Fig. 3c**. In **Fig. 4d**, the shoulder peak appears after annealing for 0.5 h at 135 °C, which is consistent with the observation from 1D-SAXS. And one can see that the shoulder peak shifts to the higher temperature side but main melting peak hardly moves as annealing time increases.

Fig. 4 Thermal stability of iPP prepared by melt crystallization (a), annealing at different temperatures for 6 h (b), annealing at 75 °C for different times (c), and annealing at 135 °C for different times (d). For clarification, the curves were vertically shifted.

Fig. 5 provides the TMDSC results of iPP. In TMDSC measurements, with a small sinusoidal modulation superimposed on the conventional linear heating program, the obtained total heat flow could be divided into a (capacity-related) reversible heat flow and a (kinetic-related) nonreversible heat flow. Generally, melting appears in not only reversible heat flow but also nonreversible heat flow, but crystallization or enthalpy relaxation can be found only in nonreversible heat flow.⁴⁹⁻⁵¹ In the reversible heat flow (**Fig. 5a** and **5b**), for both melt crystallized iPP and annealed iPP only endotherm peak could be found for all samples, which originates from the melting of the crystalline phase. As to the nonreversible heat flow (**Fig. 5c** and **d**), the situation is quite different between the melt crystallized iPP and annealed iPP. For Q10, an exothermic peak could be observed which results from the recrystallization process during the heating.^{25,40,52} It is well established that the recrystallization process occurs at the surface of the crystalline phase, where the conformational ordering of the polymer chains is higher than those in the amorphous phase. The area for the exothermic peak decreases drastically when the annealing temperature is higher than 105 °C, accompanied by the appearance of an endothermic peak. Thus, it is reasonable to infer that the melting of the newly formed crystalline phase greatly reduces the conformational ordering in the intermediate phase, which restricting the recrystallization process. This suggests that the newly formed crystalline phase should be located in the initial intermediate phase. Otherwise, the melting of the newly formed lamellae should have no influence on the recrystallization process during heating. No exothermic peak could be found for the melt crystallized iPP, suggesting that no recrystallization exists.

Fig. 5 Reversible heat flow of melt crystallized iPP (a) and annealed iPP (b), and nonreversible heat flow of melt crystallized iPP (c) and annealed iPP (d)

3.3. Mechanical relaxation behavior of iPP with different thermal history

The mechanical relaxation of iPP subjected to different thermal histories is given in **Fig. 6**. As can be seen, all the curves are characterized by multiple peaks. The peak located at ca. 0 °C is labeled as β -relaxation and the others are labeled as α_c -relaxation. It is obvious that the β -relaxation is very sharp and the α_c -relaxation is broad. For the melt crystallized samples (**Fig. 6a**), the peak temperature of α_c -relaxation (T_{ac}) keeps at ca. 84 °C when crystallization is lower than 110 °C and it increases gradually from 85 °C to 93 °C as crystallization temperature further increases. For the annealed iPP (**Fig. 6b**), the case of α_c -relaxation is especially remarkable. One broad α_c -relaxation peak could be found at 83 °C for Q10. Annealing at 45 °C shifts slightly α_c -relaxation to 84 °C. With an annealing temperature between 60 °C~90 °C, two well-separated α_c -relaxation peaks could be found. The left one is labeled as α_{c1} -relaxation and the right one is labeled as α_{c2} -relaxation. As annealing temperature increases, T_{ac2} and T_{ac1} move from 87 °C and 56 °C to 124 °C and 66 °C, respectively. When the annealing temperature is higher than 105 °C, T_{ac1} moves from 72 °C to 123 °C and the width of α_{c1} -relaxation is broadened obviously. In the meantime, T_{ac2} could not be detected. The mechanical relaxation behavior of iPP annealed at 75 °C and 135 °C for a different time is provided in **Fig. 6c** and **d**. It is worth noting that for the samples annealed at 75 °C, double relaxation peaks show up after 0.25 h. With the increase

of annealing time, T_{ac1} decreases from 69 °C to 65 °C and then keeps constantly. T_{ac2} moves from 95 °C to 103 °C after annealed for 1 h and then increases slightly to 112 °C. For the samples annealed at 135 °C, only α_{c1} -relaxation can be found, which increases from 89 °C to 94 °C.

Fig. 6 Temperature dependence of loss factor ($\tan\delta$) tested with a testing frequency of 1 rad/s for samples by isothermal crystallization at different temperature (a); by quenched and annealing at different temperature for 6 h (b); and by quenched and annealing at 75 °C for different time (c). For clarification, the curves are vertically shifted. (a'), (b'), and (c') show the peak position of mechanical α_c -relaxation for the iPP with different thermal history.

The observation of the two well-separated α_c -relaxation peaks is also reported in other studies.^{9,10,15,21,53} Traditionally, α_c -relaxation has an inter- or intracrystalline motion origin.²¹ Pulta ascribed α_{c1} -relaxation to the stress relaxation of the fraction of the noncrystalline phase containing strained molecules, and connected α_{c2} -relaxation with the viscous slip process of the crystalline elements within the noncrystalline phase.⁹ The explanation works but it is not satisfying. In our case, it has been proved by SAXS and DSC that annealing at 75 °C has a tiny influence on the crystalline phase. What really happens is the melting of imperfect lamellae, as has been evidenced by the decrease of *FWHM*. The melting of imperfect lamellae will release the constraining force not only on the polymer chains in the amorphous phase but also on the polymer chains in the intermediate phase neighboring the amorphous phase. The releasing of the constraining force results in a non-homogenous intermediate phase. Recently, a concept of “continuum of mobility” was proposed by Esposito and his coworkers.⁵⁴ The concept can be extended to a wide range of semi-crystalline polymers when the crystalline phase and the amorphous phase are strongly coupled. “Continuum of mobility” means that the relaxation of polymer chains in that phase has a broad distribution. And those polymer chains close to the crystalline phase are strongly tied and the relaxation will happen at a higher temperature. The farther the polymer chains are from the crystalline phase surfaces, the less they sense the interfacial geometrical constraints and relax at a lower temperature. Therefore, the concept of “continuum of mobility” is borrowed here to describe the relaxation behavior of the polymer chains in the intermediate phase. α_{c1} -relaxation at lower temperature side could be ascribed to the relaxation of polymer chains neighboring the amorphous phase, and α_{c2} -relaxation at higher temperature side originates from the relaxation of the polymer chains close to the crystalline phase. The shift of α_{c2} -relaxation towards higher temperature for those samples annealed at 75 °C indicates

that the conformational ordering of the polymer chain close to the crystalline phase is enhanced, which facilitates the formation of the new crystalline phase.

Combining the results from the SAXS, DSC and TMDSC measurements, the structural dependence of mechanical α_c -relaxation in the annealed iPP could be explained as follows and a schematic about the relationship between the intermediate phase and mechanical α_c -relaxation is given in **Fig. 7**. In Q10 lots of imperfect crystallites exist which could be inferred from the large *FWHM*. The polymer chains are constrained by those small crystallites. Annealing at 45 °C has negligible influence on the domain thickness. Therefore the relaxation behavior is nearly the same with Q10. With an annealing temperature of 60 °C to 90 °C, the melting of imperfect lamellae releases part of the constraining force on the polymer chains in the intermediate phase. As a consequence, heterogeneous polymer chains mobility should be expected in the intermediate phase, which giving rise to double α_c -relaxation peaks. When the annealing temperature is higher than 105 °C, initial lamellae are thickened and new crystalline phase is formed in the intermediate phase. As a result, α_{c1} -relaxation peak is broadened obviously. The peak temperature for α_{c1} -relaxation is further increased because of the enhanced conformational order of polymer chains. Moreover, the confinement in the region between the initial crystalline phase and the new crystalline phase is strongly enhanced. Therefore, α_{c2} -relaxation could not be detected unless the newly formed crystalline phase melts.

Fig. 7 A schematic about the relationship between the intermediate phase and mechanical α_c -relaxation

The activation energy of the mechanical α_c -relaxation could be obtained from the relaxation map in **Fig. 8**. For the melt crystallized iPP (**Fig. 8a**), the plot of $\ln f$ as a function of $1000/T$ could be well fitted by the Arrhenius equation:

$$f_{max} = A \exp\left(-\frac{E_{\alpha}}{kT}\right) \quad (7)$$

where A is a pre-factor, E_α is the activation energy and k is the Boltzmann's constant.

Whereas, for the annealed samples (**Fig. 8b**), a distinct transition of the slope could be found. The departure of the slope is caused by the melting of the imperfect lamellae or the newly formed lamellae. So only the lower part of the plot is employed to calculate the activation energy of annealed iPP.

Fig. 8 Mechanical relaxation map of melt crystallized iPP (a) and annealed iPP (b)

Fig. 9 demonstrates the intermediate phase thickness dependence of the activation energy of α_c -relaxation. For the melt crystallized iPP, the activation energy decreases linearly with the increase of the intermediate phase thickness, which is a result of decreased confinement force on the polymer chains. For quenched iPP, the activation energy is 53.39 kJ/mol. With an annealing temperature lower 90 °C, the activation energy decreases to 35.55 kJ/mol with the thickness of the intermediate phase increases from to 2.15 nm. Obviously, the drastic decrease of the activation energy with a small increase of the intermediate phase is caused by imperfect lamellae melting. With an annealing temperature higher than 105 °C, the activation energy decreases from 23.59 kJ/mol to 13.68 kJ/mol with the thickness of the intermediate phase increases from 2.26 nm to 2.99 nm.

Fig. 9 Activation energy of α_c -relaxation as a function of the intermediate phase thickness

4. Conclusion

In this work, the influence of annealing on the mechanical α_c -relaxation behavior of isotactic polypropylene (iPP) was investigated. The results reveal that the mechanical α_c -relaxation behavior depends strongly on the confinement force on the polymer chains in the intermediate phase. After quenching to 10 °C, abundant crystallites with a broad size distribution are formed. The polymer chains in the intermediate phase are constrained by the crystallites, giving rise to one broad α_c -relaxation peak with an activation energy of 53.39 kJ/mol. With an annealing temperature between 60 °C-105 °C, imperfect lamellae melting releases part of the constraining force, which reduces the conformational ordering of the polymer chains neighboring the amorphous phase. Consequently, two separate α_c -relaxation peaks could be observed which are labeled as α_{c1} -relaxation and α_{c2} -relaxation. α_{c1} -relaxation and α_{c2} -relaxation describe the relaxation behavior of polymer chains in the region close to the amorphous phase and the crystalline phase, respectively. Both relaxation peaks shift to a higher temperature as annealing temperature increases. In this range, the activation energy of α_{c1} -relaxation decreases drastically to 35.55 kJ/mol as the thickness of the intermediate phase increases from 2.15 nm. With an annealing temperature higher than 105 °C, a new crystalline phase is formed in the intermediate phase, which enhances the constraining force on the polymer chains. Therefore, the α_{c1} -relaxation peak is broadened and its position shifts to a higher temperature as the annealing temperature increases. Moreover, the α_{c2} -relaxation is undetectable because the polymer chains in the region between the initial crystalline phase and the newly formed crystalline phase are strongly confined. The activation energy of α_{c1} -relaxation decreases to 13.68 kJ/mol as the thickness of the intermediate phase increases to 2.99 nm.

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