The effect of high temperature annealing process on crystallization process of polypropylene, mechanical properties, and surface quality of plastic parts

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ABSTRACT: This work studied the effects and action mechanism of high-temperature annealing process parameters, such as annealing temperature, annealing duration and cooling speed, on the microstructural evolution of polypropylene (PP) on different thickness layers, the surface quality, and mechanical properties of PP plastic parts. The results show that when the PP plastic parts are annealed at slightly higher than 100°C, the resin on the surface and internal layers of plastic parts just generates the relaxation and rearrangement at the molecular level. Only at an enough high annealing temperature, the secondary crystallization and phase transformation process can be observed. The crystallinity of all annealed samples is higher than that of unannealed samples, but the crystallinity is decreased with the increase of cooling speed after annealing duration, and the annealing duration exceeding 60 min almost has no effect on the crystallinity. The microstructural change of PP on the internal layer of plastic parts is weaker than that on the surface layer. The surface hardness of the plastic parts mainly depends on the crystallinity of the surface layer, whereas the surface roughness of the plastic parts depends on not only the crystallinity, but also the space conformation of molecular chains and the residual stress. With the change of annealing process parameters, the tensile and impact strengths of plastic parts show a non-monotonic change law. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42773.

INTRODUCTION

Generally, the supermolecular structures of polymers and their distributions are greatly dependent upon the molding condition and post treatment process,[1,2] as a result of the relaxation characteristic of molecular chains, a long time is always required for polymers to transform themselves from an equilibrium state to the other equilibrium state. Inevitably, during the subsequent service period of product, the molecular chains of polymers gradually relax to achieve the thermodynamic equilibrium state. This phenomenon will result in some unpredictable changes toward the dimension stability, mechanical properties, and surface quality of product, and all of these instabilities are not to be expected.[3–5]

Annealing is a post-processing toward plastic parts at a temperature between heat deflection temperature and melting temperature (Tm) of the used resin before they are applied.[6] It has been proved that the annealing is an effective method to promote molecular chain relaxation and to induce a change of microstruc-

ture and physical properties of polymers within a relatively short time. As a kind of semi-crystalline and widely used polymorphic polymer, the crystallinity of polypropylene (PP) is relatively small and the above mentioned risk about non-equilibrium crystallization is also inevitable. Therefore, the reasonable annealing process toward PP plastic parts is significant.[3,7–9]

In the past few decades, considerable attention has been paid to the studies on annealed PP. During the annealing of PP, there may be multiple adjustment processes of microstructure, such as the elimination of internal stress, the perfection of defective crystals, the thickening and lateral growth of primary lamellae, the phase transition between different crystal forms, the relaxation and rearrangement of constrained molecular chains in amorphous phase.[10–13] When the sufficient annealing temperature and annealing duration are provided, the annealing induced secondary crystallization can be achieved, and the mechanical properties, thermal performance, and surface quality of PP plastic parts can be also optimized correspondingly.[3,14–17]

Meanwhile, some studies have also shown that low-temperature annealing contributes to the release of residual stress and the perfection of defect crystals, and high-temperature annealing favor for generating secondary crystallization and phase transformation process.[3,10,16] At present, in comparison with low-temperature annealing the investigations on crystallization state of PP and variation of application properties under high-temperature annealing process have been rarely reported.

In the annealing process, the microstructural evolution of PP is the fundamental reason causing the change of macroscopic performance of plastic parts.[7,11,13–15,18–24] Krueger et al.[25–27] found that the secondary (thinner) lamellae are formed in constrained amorphous phase regions between primary (thicker) lamellae during annealing. The investigation results given by Wang et al.[28] showed that the content increase and structural relaxation of rigid amorphous fraction (RAF) is one of the main microstructural evolution processes in annealing. Meanwhile, Li et al.[29] revealed that under the high pressure atmospheric, annealing can induce not only the evolution from β-form to α-form, but also the transition from β-form to γ-form. In addition, Bai et al.[30] found that the PP with oriented shish-kebab structure has similar change process as conventional PP during the annealing.

It is also well known that the poor impact strength is one of main reasons which restrict application of PP, fortunately, it has been widely reported that the impact strength of PP can be greatly improved by annealing treatment.[19,31,32] For example, Hedesiu et al.,[10,11] Bai et al.,[18] and Saengsuwan[26] found that the impact strength of PP, especially for β-form PP, can be sharply promoted by annealing induced perfection and rearrangement of defective crystals. Bai et al.,[18] Chen et al.,[33] and Han et al.[34] revealed that the improvement of impact strength induced by annealing treatment is mainly related to the variation of molecular chain mobility in the amorphous regions and the enhancement of β-relaxation intensity. In addition, Chen et al.[4] found that an amplified toughening effect can be achieved by introducing some microvoids into the annealed PP. Additionally, the improvement of other mechanical properties for annealed PP plastic parts always receives much concerns.[34–37]

It is not difficult to find that the studies on effects of annealing process on PP have obtained relatively deep outcomes whether in the evolution of crystallization process of PP and the improvement of mechanical properties. However, some important problems still need more concerns. First, the reported studies all cooled the samples after annealing in the atmosphere temperature, but atmosphere temperature is a variable factor, and there have been almost no studies on the different changes of microstructure and applicable properties for PP plastic parts under different cooling conditions. Second, the variation of shearing distribution, flow state and pressure condition during the melt filling process will cause the different crystallization states on the different thickness layers of plastic parts, but so far there is almost no any study on the microstructural evolution of PP with different crystallization states in annealing treatment. Third, as an important indicators for characterizing the applicable properties of PP plastic parts, the investigations on effects of

annealing process on surface quality of plastic parts are also rarely reported.

In this study, a high-temperature annealing process was selected and three different cooling methods (furnace cooling, air cooling, and water cooling) were carried out to simulate different atmosphere temperatures. Meanwhile, in order to reveal the microstructural evolution process of PP with different crystallization states in annealing treatment, the samples on the different thickness layers of plastic parts were comparatively studied. Additionally, the change law of surface quality and mechanical properties of plastic parts were also studied.

EXPERIMENTAL

Materials

The commercially available PP (T03), a kind of homopolymerized isotactic polypropylene, was purchased from Maoming branch, China Petrochemical. (China). All materials were sufficiently dried in an electric heated blast drying oven at 80°C for 8 h before implementing injection molding to erase the effect of moisture, and then they were directly molded at the received state without adding any processing agent.

Specimens Preparation

The dried PP plastic granules were molded in an XL-680 injection molding machine to obtain the standard samples. Before the annealing treatment, all samples stayed at room temperature for at least 48 h. Later on, a part of the samples were carried out annealing treatment with the temperature of 125°C, 145°C, and 165°C for 30 min, respectively. Among them, the samples with the annealing temperature of 125 and 145°C were cooled in furnace, and for the samples with the annealing temperature of 165°C, three different cooling methods (furnace cooling (low), air cooling (medium) and water cooling (fast)) were employed. Another part of samples were treated with the annealing temperature of 165°C and the different annealing durations (15 min, 30 min, 60 min, 120 min, 240 min), respectively. For convenience, all annealed samples were denoted as a code of PP-T-X, where T indicates annealing temperature and X indicates annealing duration, and the unannealed PP samples were used as reference specimens and were denoted as PP-Un. It should be noticed that all test samples were cooled in the specified condition at least 12 h after annealing, and then, were conditioned at room temperature for at least 48 h before characterizations.

Performance Testing and Characterization

XRD Test. The crystal structures of PP on the different thickness of plastic parts after annealing treatment were investigated by using a DMAX-2500PC X-ray diffractometer (WAXD, Rigaku, Japan) with a Ni-filtered Cu Kα source and an average wavelength of 1.542 A°. The equipment was operated at 45 KV and 35 mA under ambient temperature, and the scan range was between 3°and 50° with a scan rate of 2°/min.

XRD test samples were obtained from the flexural specimens with different thickness layers by using an E300CP Slicer (Exakt, German). Meanwhile, considering the discrepancy of molding process at different positions of samples in the length direction, the sampling position was strictly limited, and the sampling positions are shown in Figure 1. All test samples were processed
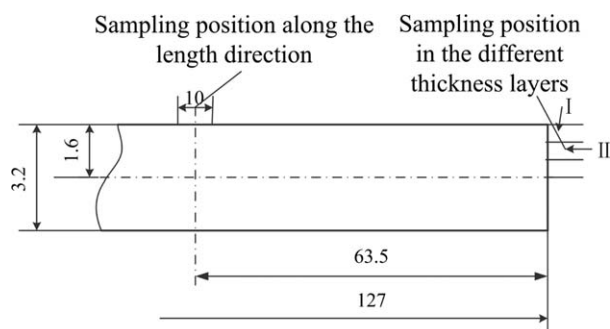
Figure 1. Schematic diagram of sampling positions for XRD test (unit: mm).

within 10 mm at the middle part of length direction on the flexural specimens. In the thickness direction, the first sampling position is at the upper surface of zone I and the second test position is situated within the zone II.

Mechanical Properties Test. The tensile and flexural properties test was carried out in a CMT2404 universal testing machine according to ASTM D 638 and ASTM D 790, respectively. The crosshead speed of machine was selected as 5.0 mm/min in tension strength test and 2.0 mm/min in flexural strength test, respectively. Additionally, a XC-5.5D electronic impact testing machine was used to measure the notched Izod impact strength according to ASTM D 256. The impact energy of 2.75 J and the impact velocity of 3.50 m/s were specified. For each test, at least five samples were measured and the average measured value is recorded.

Surface Quality Test. The surface roughness and surface hardness were tested to characterize the surface quality of annealed plastic parts. A Veeco NT9300 white light interferometer (Veeco) was employed to characterize surface roughness. The tested position was specified at the middle part of the flexural specimens in the length direction. Meanwhile, surface hardness of plastic parts was evaluated by using a XHR-150 plastic Rockwell hardness tester (Laizhou Huayin Experimental Instruments, China), and the impact samples with 6.4 mm in thickness were selected as the tested subjects.

RESULTS AND DISCUSSION

PP on surface layer of plastic parts experiences a large supercooling and temperature gradient during injection molding, which leads to a result that the molecular chains of PP on surface layer are instantaneously solidified without full relaxation, and strong directionality is generated and a large proportion of defect crystals are formed. However, PP on the internal layer begins crystallization after the filling process with full molecular chains relaxation, the small directionality is obtained, and the arrangement and stacking of molecular chains on the internal layer is also relatively perfect. As a consequence, the structure layers of PP with different crystallization state will generate different microstructural changes in the annealing process.[38–40]

Crystallization Evolution of PP on the Different Thickness Layers in Annealing Process

Crystallization Evolution of PP on the Surface Layer in Annealing Process. PP on the surface layer with strong directionality is easy to generate the microstructural evolution process during annealing, and Figure 2 gives XRD test results for PP on the surface layer with the different annealing parameters. Because the test conditions are constant and the composition of all studied specimens is same, so the diffracted intensity in XRD graph can be directly employed to analyze the crystallinity change trend of PP. The overall diffraction intensity of all crystallization phases for each plastic part with different annealing process parameters is counted from Figure 2 and the results are shown in Figure 3.

It is not difficult to find from Figures 2(a) and 3(a) that in comparison with PP-Un sample, no significant changes on the XRD curves of PP-125-30 and PP-145-30 samples are observed, neither an obvious increase in crystallinity nor phase transformation process. This phenomenon explains that though the annealing temperature has been enough high, the temperature of 145°C is still not enough to promote the phase transformation of β-PP because the melting point of β phase is higher than 145°C. At the moment, the microstructural evolution should be similar to the low-temperature annealing process, only a molecular level change can be generated and the crystallinity almost keeps constant. Due to the strong directionality of molecular chains for PP on surface layer and relatively large residual stress, in annealing process, the crystals with imperfect space conformation are easy to relax, release residual stress and transform to perfect crystals. Therefore, it can be inferred that in the early stage of the annealing process, the surface resin on PP-125-30 and PP-145-30 samples mainly generates relaxation mobility of the directional molecular chains to release residual stress and local rearrangement to achieve the perfection of defect crystals.

Additionally, the aggregating state of PP is generally divided into crystalline, the RAF and the mobile amorphous fraction (MAF), as shown in Figure 4.[3] At the later stage of duration for PP annealing below the temperature of 145°C, part of the molecule chains in MAF phase regions full rearrange, and the short helices may grow longer and new short helices may be simultaneously formed, finally, some chain segments in MAF generate the conformational ordering, and a portion of them are rearranged into more orderly interphases (RAF) and a small amount of perfect thin-lamellae. Through thus change process for microstructure, the content of RAF is enhanced and the MAF phase regions become loose. The above all changes do not involve the secondary crystallization and phase transformation processes, so the significant change of crystallinity cannot be observed during annealing of PP below the temperature of 145°C.

However, when the annealing temperature is elevated to 165°C, the crystallinity of PP on the surface layer dramatically increases, the β peak corresponding to $2\theta = 15.9°$ disappears, meanwhile, the diffraction intensity of (110), (040), (130) crystal planes for α phase corresponding to $2\theta = 13.9°$, $16.8°$, $18.4°$
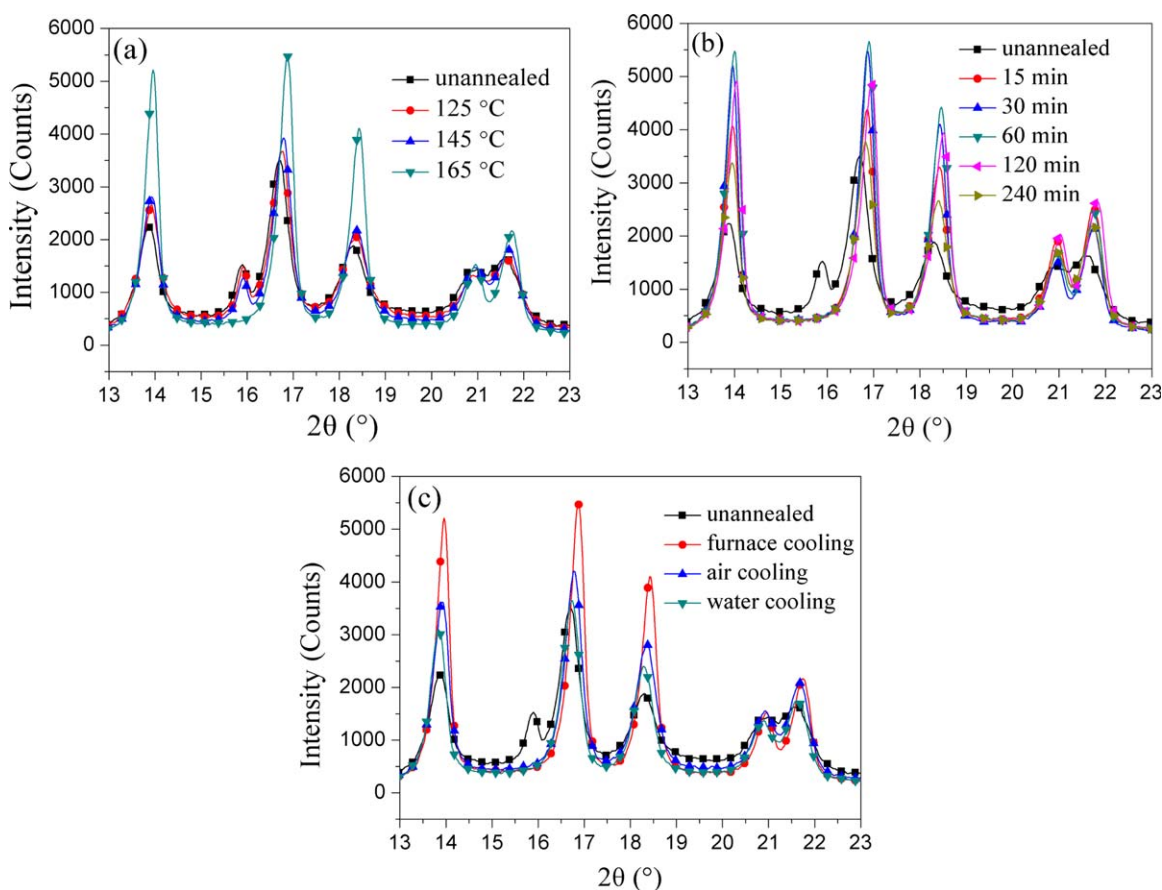
Figure 2. XRD test results for PP on the surface layer with the different annealing conditions: (a) annealing temperatures (annealing duration of 30 min and furnace cooling); (b) annealing durations (annealing temperature of 165°C and furnace cooling); and (c) cooling methods (annealing temperature of 165°C and annealing duration of 30 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

all obtain increase with different degrees, and their increasing ranges are all great. This declares that a transformation process of β phase to α phase occurs and the content of α phase increases on surface of PP-165-30 sample. Whereas, it is not difficult to find from Figure 2(a) that the content of β phase is little before annealing and it is impossible to transform to so much α phase, which implies that not only phase transformation process is generated but also secondary crystallization process from amorphous phase to crystalline phase exists on the surface of PP-165-30 sample. Generally, the melting temperature of amorphous is less than that of crystalline, and 165°C has reached the melting temperature of the selected PP. Thus, holding at 165°C for some time, more amorphous PP on surface layer of plastic parts will be melted. In the subsequent slow cooling process, the molecule chains with melting state have full time to move and rearrange, forming more new orderly thin lamellae. This is one of important reasons that the crystallinity of PP on the surface layer is significantly increased at annealing temperature of 165°C.

Furthermore, as shown in Figures 2(b) and 3(b), prolonging the annealing duration contributes to the change of crystallinity of PP on the surface layer, and the crystallinity shows the trend of the increase followed by a decrease. When the annealing duration reaches 60 min, the maximum crystallinity is obtained.

At the same time, the crystallinity of PP on surface layer of all annealed samples is higher than that of PP-Un sample. Within the annealing duration of 60 min, with the prolonging of annealing duration, more polymer matrix is melted on surface layer of plastic parts, in particular for amorphous phase. Thus, in the later cooling process, this part of resin which is mainly occupied by amorphous phase at original is cooled and is crystallized again. However, if the annealing duration is continued to prolong and exceeds 60 min, besides amorphous phase, the original crystalline phase or some favorable crystallization regions are also melted again. Though the crystallinity at this moment is still higher than that of PP-Un sample, the value of crystallinity has decreased in comparison with the result at the annealing duration of 60 min.

Traditionally, most researchers adopted environment temperature to cool plastic parts in the annealing process of PP, ignoring the temperature discrepancy in special environment. Whereas, it is not difficult to find from Figures 2(c) and 3(c) that the different cooling conditions after annealing duration will result in remarkable variation of the crystallization state of PP, and the surface quality and mechanical properties of plastic parts are correspondingly changed as well. For PP-165-30 sample, PP on surface layer with furnace cooling method has the maximum crystallinity. On the contrary, water cooling method
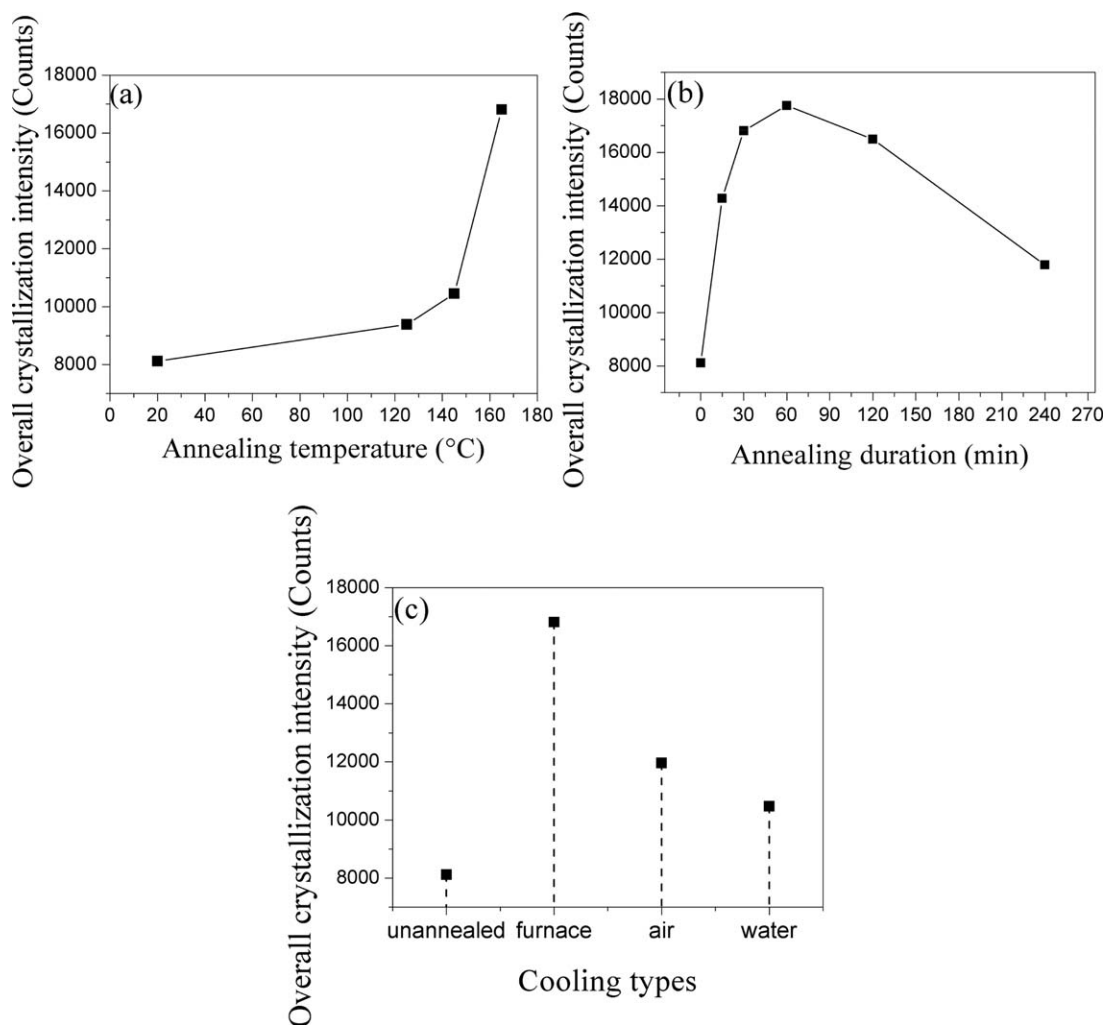
Figure 3. Overall diffraction intensity of all crystallization phases of PP on the surface layer with different annealing process parameters counted from Figure 2: (a) annealing temperatures; (b) annealing durations; and (c) cooling methods.

gives the minimum crystallinity. But the crystallinities of surface layers processed by three cooling methods are all higher than that of PP-Un sample. This explains that with the decrease of cooling speed after annealing duration, the secondary crystallization ability of melted PP is decreased. In accordance with above discussion, in annealing treatment of PP plastic parts at 165°C, the resin on surface layer, especially for amorphous phase, is easy to generate partial melting during annealing dura-

tion, and these melted resin generate secondary crystallization in later cooling process. With the increase of cooling speed, more imperfect packing density and conformational structure of molecule chains are formed again, the proportion of out-of-order arrangement regions increases and favorable crystallization regions reduce.

Crystallization Evolution of PP on the Internal Structure Layer in Annealing Process. PP on the internal structure layer locates in the regions where the resin begins to gradually crystallize after filling process. The resin in these regions occupy large ratio in whole plastic part, and they play an important role in macroscopic properties of plastic parts. But up till now, there have been almost no studies on characterizing these regions.

This article gives XRD results about the effects of different annealing process parameters on crystallization state of PP on the internal layer, as shown in Figure 5, and the overall diffraction intensity of all crystallization phases for each plastic part with different annealing process parameters is counted from Figure 5 and the results are shown in Figure 6. It can be found
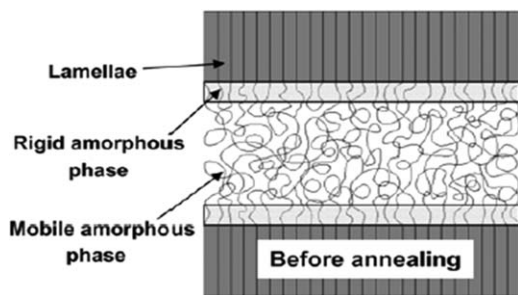

Figure 4. Schematic representations showing the microstructure of PP.[3] Please note that the figures are not drawn to scale.
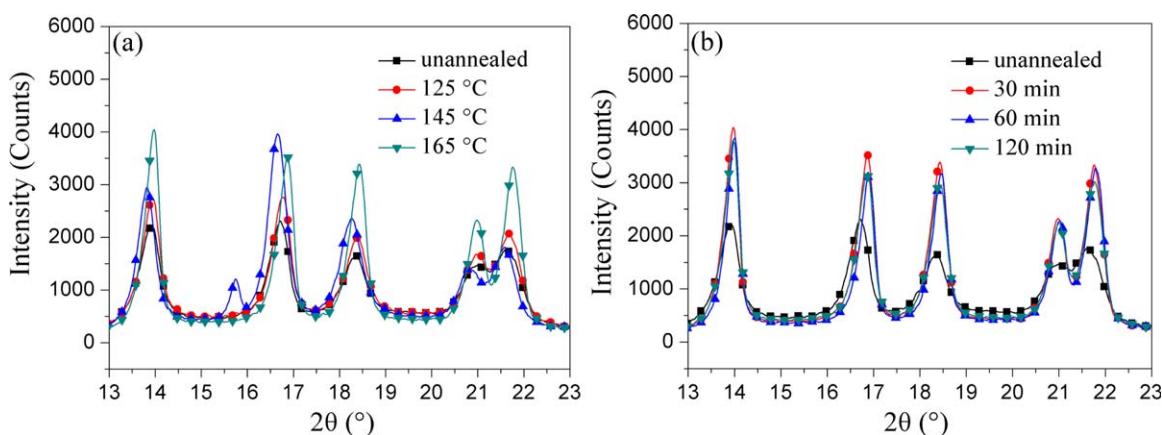
Figure 5. XRD results about the effects of different annealing temperatures and annealing durations on crystallization state of PP on the internal layer: (a) annealing temperatures (annealing duration of 30 min and furnace cooling) and (b) annealing durations (annealing temperature of 165°C and furnace cooling). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from Figures 5 and 6 that the change of crystallinity of PP on the internal layer is obviously lower than that of PP on the surface layer. In the filling process, since PP on the internal layer experiences a small shearing action, a small temperature gradient and supercooling in comparison with PP on the surface layer, the resin on the internal layer has less residual stress, and the power for the secondary crystallinity is not enough.

Similar to PP on the surface layer, the XRD curves of PP on the internal layer for PP-125-30 sample has no obvious variation, which indicates that no secondary crystallization or phase transformation occurs at this moment. However, when the annealing temperature is up to 145°C, the characteristic diffraction peak of (040) crystal plane corresponding to $2\theta = 16.8°$ on the XRD curve of the internal layer resin is significantly increased. This declares that the crystallinity of α phase increases. At the moment, though the crystallinity of PP on the surface layer has no obvious variation, owing to small shearing action and directionality experienced by PP on the internal layer, partial orderly regions which are favorable for secondary crystallinity is easy to be achieved, and the crystallinity increases slightly. For the case

of PP-165-30 sample, the crystallinity of the internal layer shows an obvious increase. It can be also seen that the diffraction intensities for (110), (040), (130), (111), and (131) crystal planes are all obviously enhanced with different degrees. Some reported literatures[3] indicated that the annealing duration of 10 min has been able to achieve a new state in microstructure of matrix. Though that is not a final equilibrium, it implies that the whole plastic part has achieved the heat uniformity for the annealing duration of 10 min. Therefore, the annealing duration of 30 min in this study can certainly attain uniform temperature distribution of PP on the surface layer and internal layer, and the resin on the internal layer also generates melting phenomenon as same as PP on the surface layer. In the slow cooling process, the molecule chains of amorphous melt rearrange and more ratio orderly stacking regions are obtained.

As shown in Figures 5(b) and 6(b), the crystallinities of samples with different annealing durations are all higher than that of the PP-Un sample. With the increase of the annealing duration, the XRD curves and the overall diffraction intensity basically keep coincidence and no prominent variation is observed. This
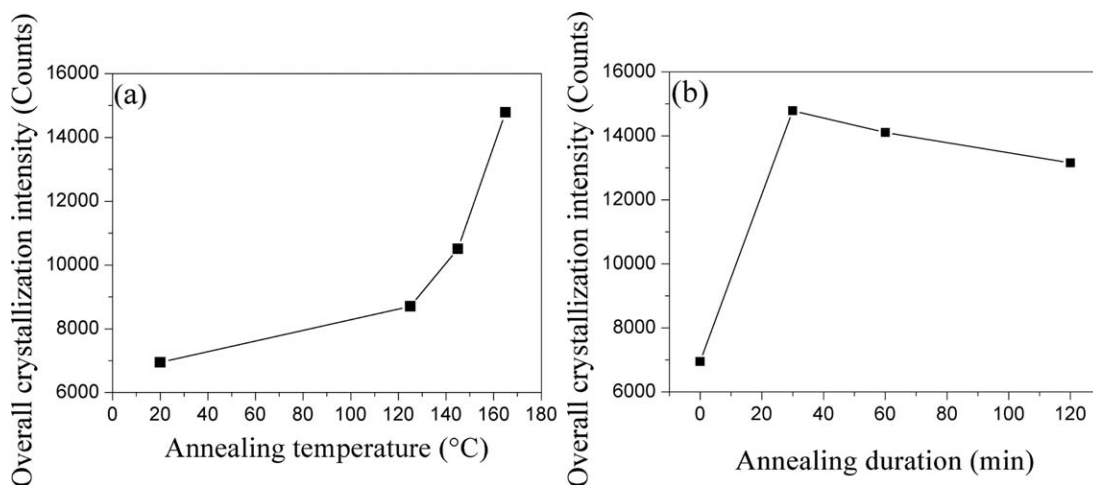

Figure 6. Overall diffraction intensity of all crystallization phases of PP on the internal layer with different annealing process parameters counted from Figure 5: (a) annealing temperatures and (b) annealing durations.

Table I. Effects of the Annealing Temperature, Annealing Duration, and Cooling Method on the Surface Rockwell Hardness of Plastic Parts

Annealing temperature (°C)	Surface hardness (HR)	Annealing duration (min)	Surface hardness (HR)	Cooling method	Surface hardness (HR)
0	95.5	0	95.5	Unannealed	95.5
125	96.7	15	105.1	Furnace cooling	105.8
145	99.7	30	105.8	Air cooling	103.2
165	105.8	60	105.8	Water cooling	102.3
		120	104.8		
		240	104.7		

indicates that the annealing holding time of 30 min is enough for the microstructural change of PP on the internal layer. This phenomenon is different from that of PP on the surface layer. According to the above discussion, under the annealing temperature of 165°C and annealing duration of 30 min, the whole plastic part reaches a thermal equilibrium state, and the crystallinity of PP on the internal layer is significantly increased. However, when the annealing duration is prolonged, though more amorphous phase is melted and recrystallized, more favorable crystallization regions are also simultaneously melted because of slow heat dissipation of resin located on the internal layer. These two action processes realize the complementary, leading to the result that the crystallinity of PP on the internal layer basically maintains balance for the longer annealing duration.

Relationship Between Crystallization State of PP and Surface Quality of Plastic Parts

The surface quality of plastic parts is an important indicator measuring their application. It usually includes the surface hardness, the surface roughness, surface glossiness, and chromatic aberration, and so on. Based on the discussion in "Crystallization Evolution of PP on the Different Thickness Layers in Annealing Process" section of this article, the annealing temperature, annealing duration, and cooling method have different effects on the crystallization state of PP on the surface layer, and thereby result in the corresponding change of surface quality.

Effects of Annealing Processes on Surface Hardness of PP Plastic Parts. Table I gives the effects of the annealing temperature, annealing duration, and cooling method on the surface Rockwell hardness of plastic parts. It can be seen that with the increase of the annealing temperature, the surface Rockwell hardness of plastic parts monotonically increases. In comparison with PP-Un sample, the value of surface Rockwell hardness for PP-165-30 sample is increased by 10.8%. Referring to the above discussion about the crystallization state of PP located on the surface layer, though the crystallinity of PP on the surface layer has no significant change below the annealing temperature of 145°C, some short helices in the molecule chains of MAF regions grow longer and new short helices are simultaneously formed, and the proportion of RAF is drastically increased. These reasons all contribute to the improvement of the surface Rockwell hardness of plastic parts. When the annealing temperature of 165°C is employed, PP located on the surface layer

generates not only phase transformation, but also secondary crystallization process. Thus, the content of rigid α phase is dramatically increased, and the surface Rockwell hardness of plastic parts is further improved.

In addition, with the increase of annealing duration, the surface Rockwell hardness of PP plastic parts shows a trend of the increase followed by a decrease, but this variation gradually becomes unobvious after the annealing duration of 15 min. This may be because that with the increase of annealing duration, the crystallinity of PP on the surface layer of plastic parts first increases, and then decreases. Though the surface hardness of plastic parts is generally proportional to the crystallinity of polymers, when the secondary crystallization occurs, the MAF regions become more and more loose and their mobility is gradually enhanced. This effect is negative for the surface hardness of plastic parts. Therefore, the combination action of above two factors results in a small change of the surface hardness after the annealing duration of 15 min.

For the different cooling methods after annealing treatment, the surface hardness corresponding to three samples is all higher than that of PP-Un sample. With the increase of cooling speed, the surface hardness of plastic parts gradually decreases. This is not only consistent with the test result of XRD in Figures 2(c) and 3(c), but also inseparable with the residual stress caused by fast cooling speed.

Effects of Annealing Processes on Surface Roughness of Plastic Parts. The surface roughness is an intuitive response for the surface micro geometric feature, essentially, it is also closely bounded up with the microstructure of PP on the surface layer. In this study, the test results both along X profile and Y profile of the samples are simultaneously given, and the comprehensively evaluated value (Ra) of surface roughness is also presented at top of the corresponding figures.

Figure 7 gives the change law of surface roughness for PP samples with different annealing temperatures. It can be seen that the value of Ra increases with the increase of annealing temperature. This indicates that the surface of plastic parts becomes rougher and rougher. Generally, the increase of crystallinity of PP represents more orderly arrangement regions of microstructure to be formed in its matrix and this is favor of the reflection of light, and the roughness degree of plastic part surface should be supposed to decrease. However, for a macro perspective,
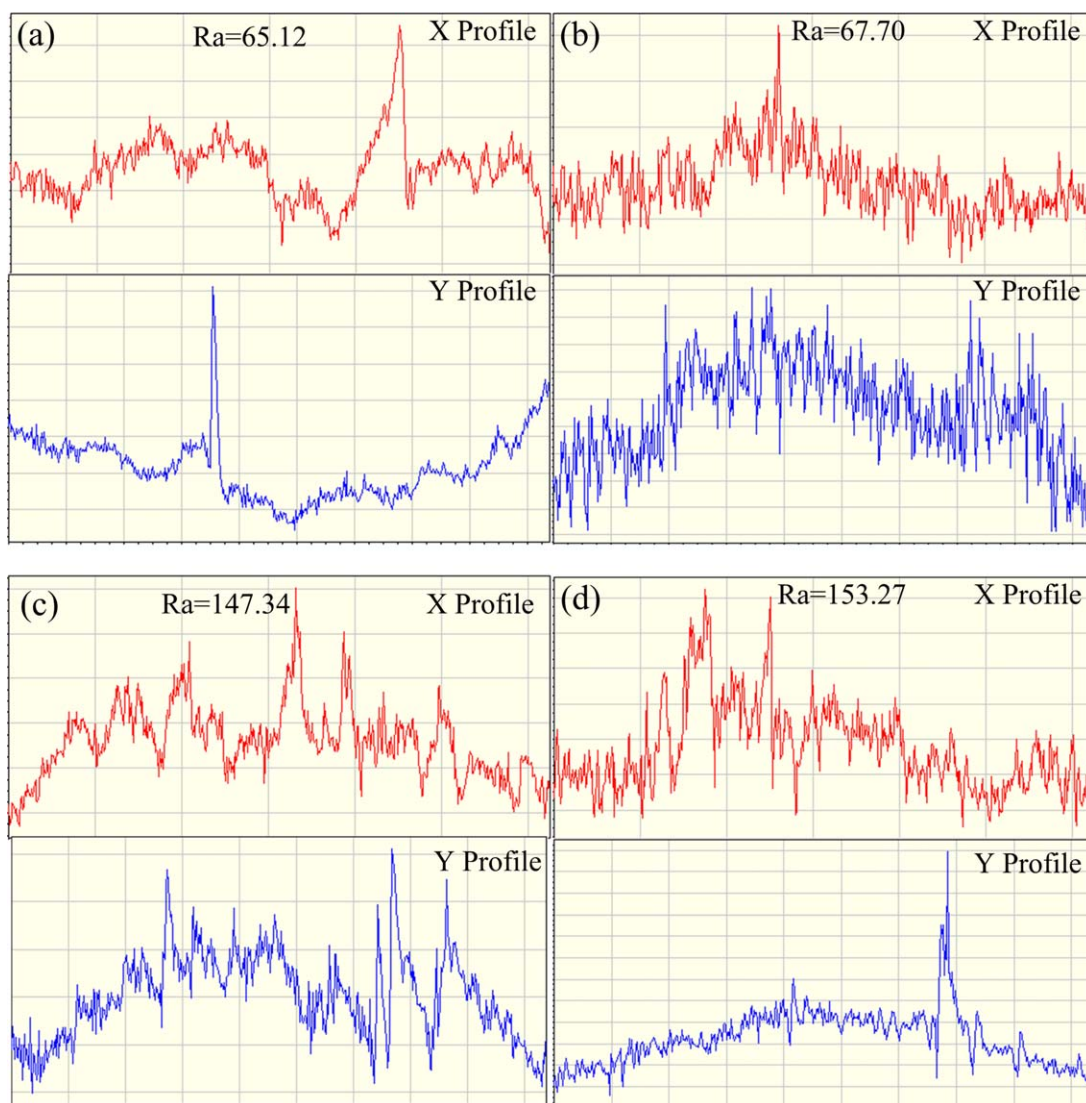
Figure 7. Change law of surface roughness for PP samples with different annealing temperatures, annealing duration of 30 min and furnace cooling condition: (a) PP-Un; (b) 125°C; (c) 145°C; and (d) 165°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

there is not distinct boundary to be observed between the crystalline regions and amorphous regions in PP plastic parts, and these two regions merge to each other and it is difficult to clearly distinguish them. During the annealing, the molecule chains in amorphous regions relax and arrange, forming more rigid RAF and crystallizing into crystal lamellae. These newly formed RAF and crystal lamellae randomly distribute in the original crystal phases, though they are regularly arranged for themselves, it is hard for them to comply with the space conformation of the original crystals. As a consequence, the value of surface roughness under the optical condition increases with the increase of annealing temperature.

Figure 8 shows the effects of annealing duration on the surface roughness of plastic parts. The values of Ra of samples are all higher than that of PP-Un sample with different annealing durations, that is, their surface becomes rougher and rougher. The reason causing this phenomenon is consistent with that of annealing temperature. However, with the increase of annealing

duration within 120 min, the Ra value of plastic part surface gradually decreases. This may be because that when the annealing duration is prolonged, the molecule chains of PP on the surface layer can fully relax, and the crystallinity increases. The full relaxation time contributes to better consistency of space conformation between secondary crystals and original crystals, and finally the surface of plastic parts become smoother. On the contrary, when the annealing duration is prolonged continuously, the surface of plastic parts is not smoother, but rougher. According to the test results shown in Figures 2(b) and 3(b), at this stage, the crystallinity of PP located on surface layer decreases and amorphous ratio increases, and finally the value of Ra magnifies.

By using the different cooling speeds after annealing duration, the surface roughness of plastic parts with a large discrepancy is obtained, and their values are all higher than that of PP-Un sample, as shown in Figure 9. By comparing Figure 9(b,c), it can be seen that the Ra value of the sample obtained by air cooling method is lower than that of the sample obtained by
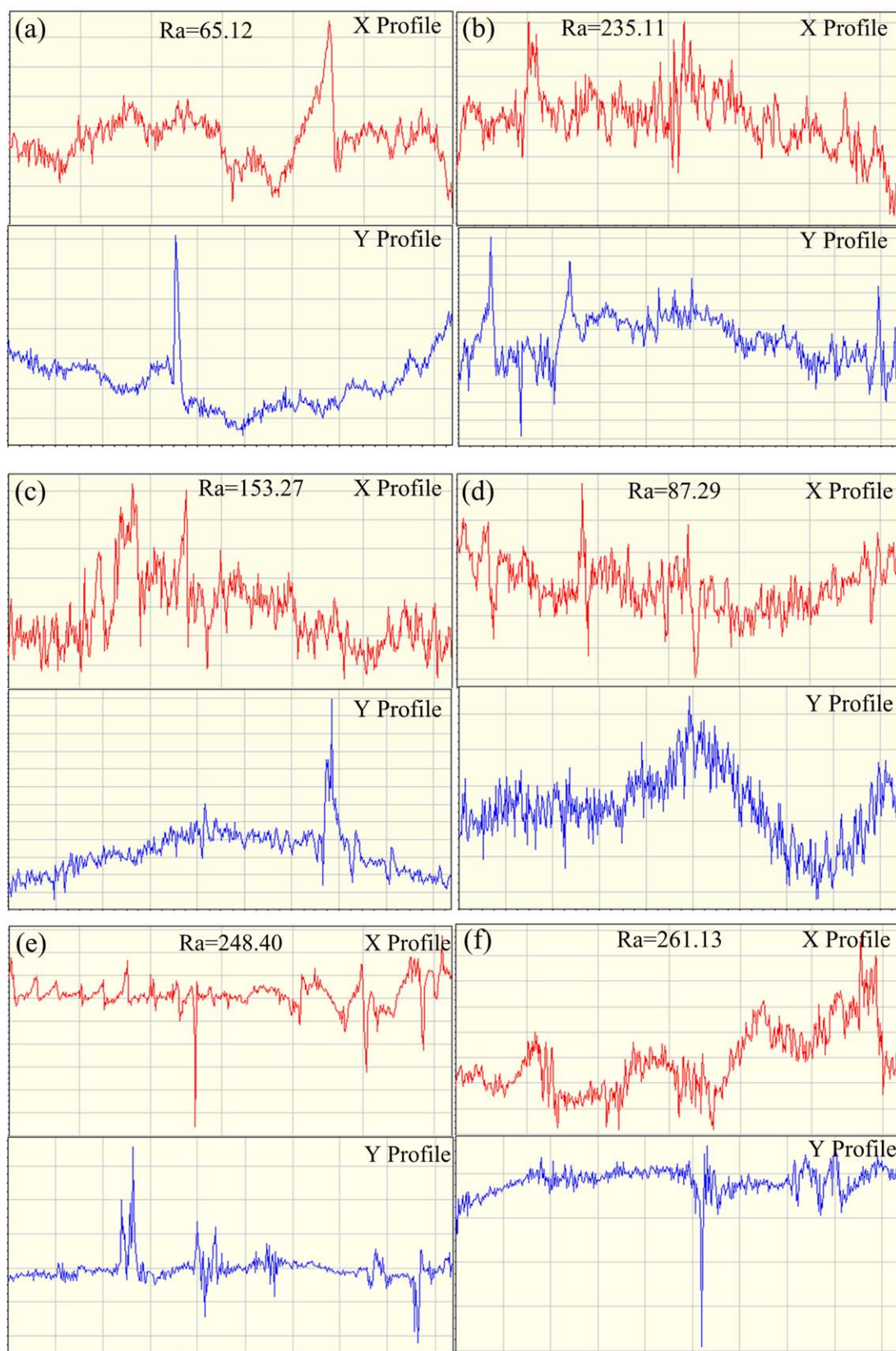
Figure 8. Effects of annealing durations on the surface roughness of plastic parts with annealing temperature of 165°C and furnace cooling condition: (a) PP-Un; (b) 15 min; (c) 30 min; (d) 60 min; (e) 120 min; and (f) 240 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
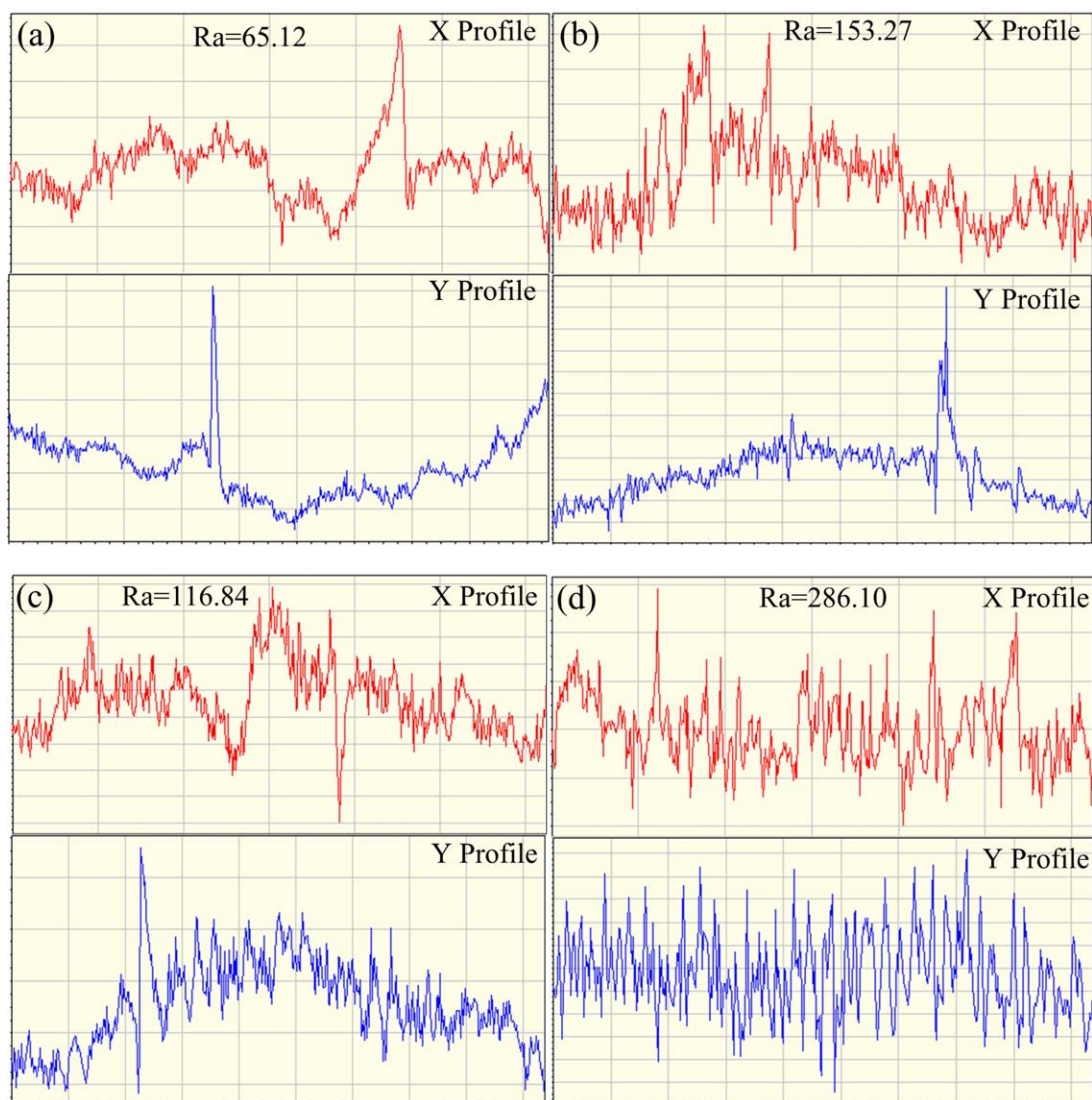
Figure 9. Surface roughness of plastic parts under different cooling speeds with annealing temperature of 165°C and annealing duration of 30 min: (a) PP-Un; (b) furnace cooling; (c) air cooling; and (d) water cooling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

furnace cooling. In accordance with the above discussion, when the air cooling method is adopted, the crystallinity of PP on the surface layer is smaller than that obtained by furnace cooling, the proportion of secondary crystals with abnormal space conformation is also decreased, resulting in a larger decline of Ra in air cooling than in furnace cooling. However, when the water cooling way is employed, though the crystallinity of resin continues to decrease and the proportion of secondary crystals with abnormal space conformation reduces, the fast cooling speed of water cooling leads to a large residual stress in the surface layer of plastic parts, meanwhile, the cooling water may cause a certain contamination of plastic part surface. Therefore, the surface of plastic parts with water cooling way becomes rougher.

Effect of Annealing Process on Mechanical Properties of PP Plastic Parts

The improvement of mechanical properties of plastic parts is one of main purposes for the annealing treatment, and it has

also attracted much interest of researchers.[31,32,34–37] Figure 10 gives the effects of annealing temperature and annealing duration on tensile strength and notch impact strength of PP plastic samples. Based on the discussion in "Crystallization Evolution of PP on the Different Thickness Layers in Annealing Process" section, when the samples are annealed at 125°C, the release of residual stress, perfection of defect crystals are both generated in PP on both the surface and internal layers, and these changes are beneficial to the improvement of the spherulites and the enhancement of the boundary strength.[34] Thus, in the universal tensile process, the stress transfer becomes easier and the stress distribution is more uniform in matrix. When the annealing temperature reaches 145°C, PP on the surface layer still continues the above change process, yet PP on the internal layer begin emerging the secondary crystallization process, and the tensile strength increases continuously. If the annealing temperature continues to increase, the secondary crystallization and phase transformation processes are observed in both two structure
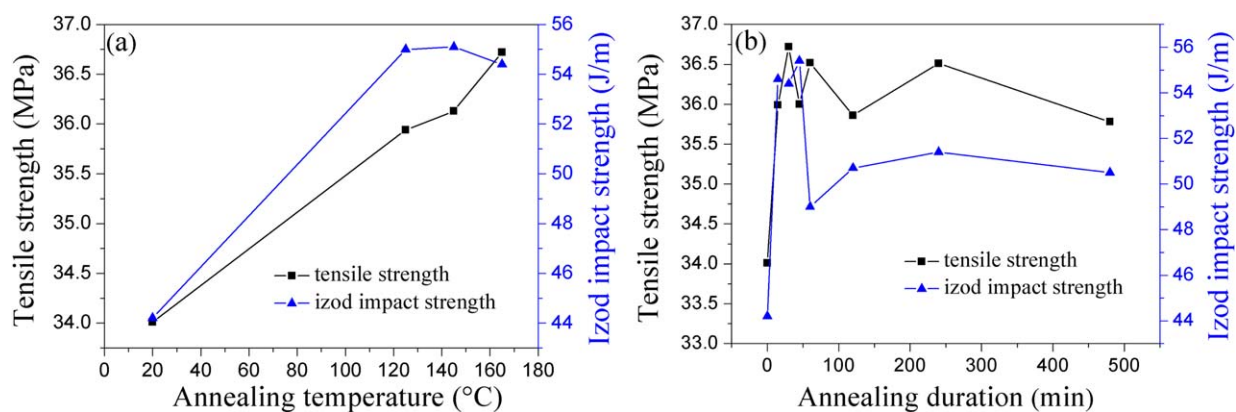
Figure 10. Effects of annealing temperature and annealing duration on tensile strength and notch impact strength of PP plastic parts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

layers, and the tensile strength is further enhanced. On the other hand, with the increase of annealing duration within 30 min, the molecule chains of matrix get full relaxation, the crystallinity increases gradually and the tensile strength is improved too. But when the annealing duration continues to prolong, though the crystallinity still increases, MAF in amorphous areas becomes looser and easier to move, and the tensile strength keeps balance.

As shown in Figure 10, in comparison with the PP-Un sample, the impact strength of the annealed samples is all increased with different degrees. With the increase of annealing temperature, the impact strength firstly increases, and then basically keeps balance after a brief decrease. When the PP plastic parts are annealed at 145°C, the increase of the impact strength may be because that the perfect crystals provide larger resistance to plastic deformation than relatively imperfect crystals. It is believed that the reduced density for MAF in amorphous regions and increased thickness of RAF also partly contribute the improvement of the impact strength. However, when the annealing temperature is continued to rise, PP matrix begins to generate the secondary crystallization and phase transformation process. The thickness of the original crystal lamellae increases, the ductile β phase transforms into brittle α phase and some new thin lamellae appears. These changes make the impact strength decrease slightly.

In addition, it can be seen from Figure 10 that with the increase of annealing duration within 45 min, though the crystallinity of matrix is increased in this stage, the perfection of defect crystals and release of residual stress contribute to the obvious increase of impact strength. When the annealing duration continuously increases, the above change becomes unapparent and the impact strength tends to constant. Ritchie et al.[41] believed that the

repeated nucleation of such dislocations from interfaces between lamellae and amorphous layers determines the fracture process. In other words, the ability of chain slipping in the amorphous regions also influences the degree of the plastic deformation in the semi-crystalline polymers.

Furthermore, the effect of cooling speed after annealing duration on the mechanical properties of plastic parts cannot be ignored too. Table II shows the effect of the cooling speed after annealing duration on the mechanical properties of plastic parts. With the increase of cooling speed after annealing duration, the tensile strength presents a trend of the increase followed by a decrease, but this change is inconspicuous. However, at this stage, the impact strength of plastic parts decreases sharply, which can be interpreted by the discussion in "Crystallization Evolution of PP on the Different Thickness Layers in Annealing Process" section.

CONCLUSIONS

1. On account of intense directionality and residual stress, PP on the surface layer is easier to generate the microstructural evolution process during annealing than that on the internal layer. However, since the amount of PP on the internal layers is much larger than that on the surface layer, the microstructural evolution of PP on the internal layers on mechanical properties of plastic parts cannot be ignored.
2. When the annealing temperature is slightly higher than 100 °C, the molecular chains are easier to relax, rearrange, or generate the evolution of microstructure at the molecular level. Only for an enough high temperature, the secondary crystallization and phase transformation process can be observed.

Table II. The Effect of the Cooling Speed After Annealing Duration on the Mechanical Properties of Plastic Parts

Cooling speed after annealing duration	Unannealed	Furnace cooling	Air cooling	Water cooling
Tensile strength (MPa)	34.01	36.72	38.95	35.37
Impact strength (J/m)	44.2	54.4	36.4	19.1

3. Besides the crystallinity of PP, some other factors, such as the value of residual stress, content of RAF, mobility ability of MAF, and the repeated nucleation in molecular dislocations regions, are also important ones affecting the surface quality and mechanical properties of plastic parts.

4. In order to obtain PP plastic parts with excellent comprehensive performance, a relatively high annealing temperature and small cooling speed should be selected. Meanwhile, an annealing duration of 60 min is enough for achieving the required crystallization state and application properties.

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