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Influence of reprocessing on the crystallization of polypropylene in PP/PA6 blends

Summary — The non-isothermal crystallization processes of polypropylene (PP) in PP/PA6 blends were investigated by the differential scanning calorimetry method (DSC). The blends containing 20 wt. % of PA6 were prepared in a single-screw extruder. The blends were reprocessed ten times under the same conditions. DSC measurements were used to analyse of thermal properties and overall crystallization parameters of PP in the presence of PA6. In this work, the extent of crystallization, the half-time of crystallization as well as melting and the crystallization peak temperatures were determined. It was found that the crystallization temperature of PP remained practically unaltered after 2–8 extrusion processes, whereas further reprocessing (tenth time) induced significant changes in the T_{cp} value. However, a strong effect of the enhancement of polypropylene crystallization rate was observed in relation to the nucleating action of repeated extrusions. The extent of crystallization increased and the half-time of crystallization decreased according to successive reprocessing cycles. The interpretation of this difference in crystallization parameters after reprocessing of the blends is analyzed according to thermooxidation or thermo-mechanical degradation processes.

Key words: polypropylene, polyamide-6, blends, crystallization, processing, recycling.

WPLYW PONOWNEGO PRZETWARZANIA NA KRYSZALIZACJĘ POLIPROPYLENU W MIESZANINACH PP/PA6

Streszczenie — Przedstawiono wyniki badań krystalizacji polipropylenu w mieszaninach z poliamidem-6 przeprowadzone z wykorzystaniem techniki skaningowej kalorymetrii różnicowej (DSC) (rys. 1, 2, 3). Mieszaniny PP/PA6 zawierające 20 % mas. PA6 otrzymywano metodą wyłaczania. Uzyskane stopy poddano 10-krotnemu przetwórstwu. W badaniach kalorymetrycznych wyznaczono parametry kinetyczne procesu krystalizacji — stopień konwersji fazowej i połówkowy czas krystalizacji (rys. 3, 4). Ponadto określono wartości temperatury przemian fazowych. Nie stwierdzono zmiany temperatury krystalizacji PP w mieszaninie aż do ósmego cyklu przetwórstwa. W próbkach przetworzonych dziesięciokrotnie temperatura krystalizacji znacznie wzrosła. Zaobserwowano duży wpływ powtórnego przetwórstwa na zwiększenie szybkości krystalizacji polipropylenu w badanych mieszaninach. Wielokrotność procesu wyłaczania spowodowała wzrost stopnia konwersji fazowej i skrócenie połówkowego czasu krystalizacji. Przedstawione wyniki dyskutowano w kontekście przemian termooksydacyjnych oraz degradacji termomechanicznej, zjawisk zachodzących w stopie poddanym wielokrotnemu recyklingowi.

Słowa kluczowe: polipropylen, poliamid-6, mieszaniny, krystalizacja, przetwórstwo, recykling.

Mixing of polymers attracts a growing interest of scientists concerned with the development of new materials. Polymer blending is a way of tailoring of product properties to specific applications as an alternative to direct synthesis of new polymeric materials. In many cases, it is not enough to combine two incompatible polymers in order to obtain desirable properties [1–3]. However, in any situation where two polymers come into contact to produce polymer blends, alloys or multilayer films, a possibility to reach a synergistic properties combination depends on the adhesion of constituents. The mechanical behavior and morphology of blends depend not only on the properties of

each component but also on the interface. The interface is a result of the chemical and physical interaction between both polymers. It was found that polyamide-6 (PA6), being the dispersed phase, could be fibrillated in polypropylene (PP) matrices and the fibrillation occurred in the channel of the extruder. The notched impact strength of PP/PA6 blends increased with increasing content of PA6, while the tensile strength decreased [4]. In PP/PA6 blends, maleic anhydride grafted or chemically modified polypropylene types are usually applied as compatibilizers [5–7]. Moreover, in most cases, block copolymers are used as compatibilizing agents [8].

In polymer blends, where one of the components is a semicrystalline polymer, the presence of the second component has a considerable influence on the crystallization process. Crystallization kinetics of a semicrystalline polymer in the blend system is very complex and strongly depends on the content of components, the processing conditions, the adhesion between polymers, the thermal history and the dispersion of the components.

The mixing of immiscible polymers, when one of the components is used in part equal 80 % or more, yields a characteristic morphology with very fine dispersions [9, 10]. For the PP/PA6 blends, an additional aspect is noted: the presence of two crystallizable components. In this case, the crystallization-induced structural changes offer additional advances for the controlled modification of the polymer properties [8].

The efficiency of the nucleation process in crystallizable polymers usually consists of one or more of the following phenomena: homogeneous nucleation, heterogeneous nucleation or self-nucleation. In the case of immiscible matrix of polymer blend, the nucleation of semicrystalline polymer in the bulk is subdivided into isolated regions [11]. The problems of crystallization kinetics as well as of specific features of PP/PA6 mixtures were discussed in many studies [1, 5, 11–13]. It is known from the literature data that PA6 acts as a heterogeneous nucleating agent for iPP and enhances the rate of crystallization of iPP. Moreover, a transcrystalline layer is formed on the surface of PA6 dispersed in polypropylene matrix as droplets or fibers embedded in to the iPP melt induce the nucleating effect of PA6 [14–19]. These investigations were done with the use of non-recycled blends only. Up to now, the influence of PA6 on the crystallization of PP in a multi-recycled PP/PA6 blend has not been studied yet.

Material recycling is the most common technology used to handle post-consumer and post-production polymeric waste and it leads to irreversible changes in the mechanical properties and structures of the materials, due to high temperatures, high pressures and shear forces applied. The polypropylene constitute approximately 12 % of the plastic waste in Europe.

Although numerous articles have been published describing the study of the thermal stability of polypropylene, a few efforts have been devoted to the study of degradation of recycled polypropylene blends. The different chemical structures of components in a blend (like PP and PA6) may change adhesion. The compatibility of components can be affected by the presence of polar groups produced during thermooxidation process [20].

In this work, we present an experimental study of the crystallization of multi-extruded recycled polypropylene in the presence of polyamide-6, using differential scanning calorimetry (DSC). Moreover, DSC investigation is an effective method to estimate the degradation of PA6 in recycled materials [21]. Changes in the crystallization rate in relation to times of reprocessing of the

blends have been studied. This paper would be essential for broadening knowledge about nucleation ability of components in multi-recycled blends. It is very important because the changes of the nucleating efficiency are essential for determination of real conditions in polymer processing (e.g. the value of injection molding cycle time).

EXPERIMENTAL

Materials

The isotactic polypropylene (iPP) and polyamide-6 (PA6) used in the experiment are commercial products. PP (Malen PF-401) was purchased from the Petroleum Chemical, Orlen Plock, Poland and PA6 (Tarnamid T-27) was purchased from the Z.A. Mosciwe-Tarnow, Poland.

Preparation of PP/PA6 blends

The blends containing 20 wt. % of PA6 were prepared in a single-screw extruder [diameter (D) = 25 mm, L/D = 25; screw length (L)]. The temperatures of feeding zone, melting zone, compression zone and the die were 150, 240, 250 and 230 °C, respectively. The screw rotational speed ranged from 25 to 30 rpm. The extrudate was cooled in water at 20 °C and then pelletized into granules. Next, the granules were dried in an oven for 24 h at 60 °C.

The blends were reprocessed ten times under the same conditions.

Differential scanning calorimetry (DSC) measurements

Thermal analysis was performed using a Netzsch Differential Scanning Calorimeter, model DSC 200, under argon atmosphere. The instrument was calibrated with an indium standard. For non-isothermal crystallization investigations, the samples were first heated to 240 °C, and kept at this temperature for 2 min to eliminate the previous thermal and/or mechanical history. Then, the samples were quenched to 40 °C at the rate 5 °C/min. This procedure was repeated two times and the second tour was used in the calculations.

DSC measurements were used to analyse the thermal properties and overall crystallization parameters of PP in the presence of PA6. In our experiments, the extent of crystallization and half-time of crystallization were determined. On the basis of the values determined for the enthalpy of crystallization (H), the extent of crystallization, α was calculated:

$$\alpha = \frac{\int_0^t (dH/dt) \cdot dt}{\int_0^{t_k} (dH/dt) \cdot dt} \quad (1)$$

where: t — time of crystallization; t_k — final time of crystallization.

On the basis of the curves of α versus time, the half-time of crystallization ($t_{0.5}$) was determined as the time at 50 % extent of crystallization.

Moreover, the melting and the crystallization peak temperatures T_{cp} of the blends were obtained from the maxima of endothermic and exothermic peaks, respectively.

RESULTS AND DISCUSSION

Melting and crystallization temperatures

Figure 1 illustrates typical DSC thermograms of crystallization of pure PP and PP/PA6 blends.

The blends displayed two single peaks at the temperatures corresponding to the crystallization of pure polymers. DSC thermograms obtained after non-isothermal crystallization represent remarkable differences. An increase in the crystallization peak temperature by about

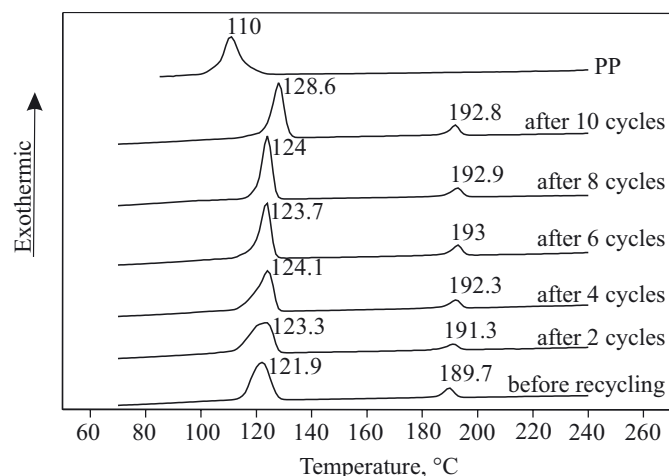


Fig. 1. DSC thermograms of nonisothermal crystallization of pure iPP and PP/PA6 blends

12 °C was observed for PP in the blends before reprocessing in comparison with pure PP. Consequently, it can be suggested that PA6 acts as a heterogeneous nucleation agent in polypropylene matrix. According to Fig. 1, the DSC traces of PP and PA6 remained practically unaltered after 2–8 extrusion processes and have similar values of T_{cp} in the range of 123–124 °C. It is very interesting that further reprocessing (tenth time) induced significant changes in the T_{cp} value. In this case, the influence of reprocessing of blends can be evaluated by the shifting of DSC exothermic peak towards higher temperature by *ca.* 5 °C. The observed changes in T_{cp} values may be a result of the arrangement of the shorter polymer chains formed as a consequence of reprocessing. It is well known that reprocessing of polymers is responsible for the cutting of polymer chains. Consequently, the

crystallization of shorter chains proceeds easier. The shifting of T_{cp} peaks was not observed in the reprocessed PA6, as the values in the range of 191–193 °C after each extrusion were noticed.

Similarly as in the case of crystallization temperature, the values of the degree of crystallinity depend on the number of reprocessing cycles. In the PP/PA6 mixtures reprocessed 2, 4, 6 and 8 times, the degree of crystallinity of polypropylene ranges from 43–45 % and is comparable with the value calculated for the system which is not subjected to recycling. On the other hand, in the case of the mixture recycled 10 times, a distinct increase in the degree of crystallinity of polypropylene (about 51 %) was observed. It is worth to notice that the degree of polyamide crystallinity remains unchanged for all the examined systems reaching approximately 30 %.

Moreover, all the blends have similar values of melting temperatures in the range of 167–169 °C (for PP) and of 214–222 °C (for PA6). However, as we can see from Figure 2, maximal melting peak temperatures of PA6 are included in a larger range.

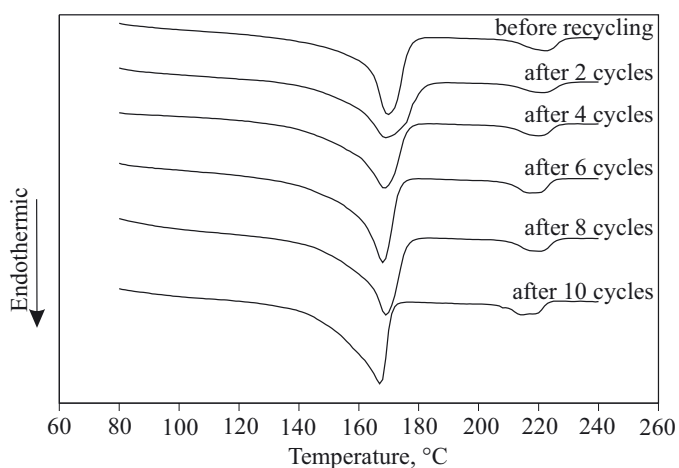


Fig. 2. DSC thermograms of melting process of multi-extruded PP/PA6

This phenomenon is observed, in particular, for the samples recycled six as well as more times. This fact may indicate that in the multi-recycled PP/PA6 blend, the fractions of polyamide chains of different lengths, formed during the processes of mechanical and thermal degradation, are present. This molecular polydispersity of polyamide chains may influence the crystallization process of the polypropylene matrix.

The differences in the crystallization temperature values may be associated with differences in the length of polymer chains. The differences in length result from the application of consecutive reprocessing cycles. The process of polymer crystallization should be considered taking into account two stages: nucleation and growth of crystallites. On the one hand, it should be expected — in accordance with the Gibbs-Thomson equation — that

the crystallization of long fragments should take place at higher temperatures [22]. Experiments carried out by Carvalho [23] confirm the observation that polypropylene of the highest molecular weights has the highest overall crystallization rate, probably due to the contribution given by a high nucleation rate because its growth rate was the lowest.

On the other hand, in general, both the overall rate of crystallization and the resulting crystallinity decrease with increasing molecular weight [24, 25]. Moreover, Chen et al. [26] observed that the crystallization rate of poly(trimethylene terephthalate) (PTT) decreased with the increase in molecular weight of PTT. They showed also that the crystallization temperature increased with the decrease in molecular weight of the polymer. Similar observations were registered in the experiments presented in this study.

Extent of crystallization of polypropylene matrix

The extent of crystallization (α) for PP and PP/PA6 blends versus crystallization time is shown in Figure 3.

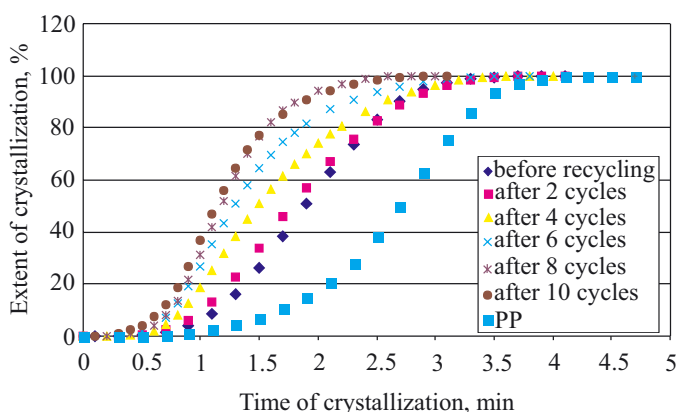


Fig. 3. Extent of crystallization of pure iPP and in the blends with PA6

The extent of crystallization of PP at a given time is significantly higher in the blends than in pure PP. The observed differences between the blends and pure polypropylene might obviously be attributed to the predominant nucleating effect of PA6. Moreover, the extent of crystallization strongly depends on the number of repeated extrusion processes. A strong effect of the enhancement of PP crystallization rate is observed in relation to the repeated extrusions. The extent of crystallization increased with the increase in the number of reprocessing cycles.

Half-time of crystallization of polypropylene

Figure 4 shows the half-time of polypropylene crystallization for pure PP and PP/PA6 blends.

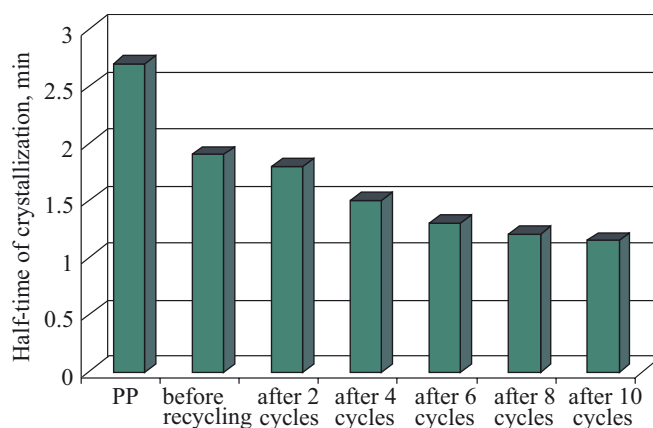


Fig. 4. Half-time of crystallization of multi-extruded PP/PA6 blends

The half-time of PP crystallization in the blends was shorter (ca. 30–60 %) than that of pure PP. This observation confirms the nucleation process of PP in the presence of PA6 domains dispersed in the polypropylene matrix. With the increasing number of reprocessing cycles, the differences among the values of half-time of crystallization of PP/PA6 blends and pure PP increased. Figure 4 clearly shows that the half-time of crystallization decreased with the number of reprocessing cycles. From the above results it can be concluded that repeated extrusion of PP/PA6 blend acts as a nucleating process for PP.

The interpretation of these differences in the extent of crystallization and half-time of crystallization of the blends depends on some phenomena. This may be analyzed according to thermooxidation or thermo-mechanical degradation processes.

In the PP/PA6 blend, PP and PA6 are immiscible, not only in the thermodynamic sense but also practically, and PP forms large separated phase in which the nuclei might be available for crystallization. The crystalline PA6 particles could act as nuclei for PP crystallization. An explanation of these changes in the extent of crystallization and half-time of crystallization may be connected with a decrease in thermal stability of polypropylene. Camacho and Karlsson [27] reported earlier that polypropylene showed a decrease in thermal stability up to the third extrusion. Moreover, La Mantia and Mongiovi [20] noted that the degradation occurring in PP may change the interface between the components of the blend by the presence of species produced during thermooxidation, e.g. carbonyl groups. In this case, these species may act as compatibilizing agents. Based on the above discussion, we suggest that the influence of the chemical composition of a polymer (modified by the processing cycles) on the nucleation ability and crystallization rate is evident. In the present study, the shortest half-time of crystallization and the highest crystallinity degree were observed for PP/PA6 blends recycled 10 times. It can be assumed that these blends were mostly

subjected to thermooxidation reactions which caused an improvement in the compatibility between the component polymers due to the appearance of functional groups. Despite the extensive investigations dedicated to thermal stability and viscoelastic properties of multi-extruded polyolefins and their blends [28–30], the final effect of reprocessing on the crystal structure, stability and properties of such materials is difficult to predict and many questions remain with no answer [31].

However, it is possible to observe some impact of the compatibility change caused by the thermooxidation processes on the crystallization of polyolefin mixtures subjected to multiple extrusion. Camacho et al. [27] reported that the increase in crystallinity may be a result of the rearrangement of shorter polymer chains formed as a consequence of the chains scission that probably occurred during reprocessing. In the case of the systems examined in this study, the observed significant increase in the degree of crystallinity of polypropylene in the mixtures subjected to 10-fold extrusion can be also attributed to the chains scission. This increase in compatibility resulting from the enhanced intermolecular interactions could have caused a higher crystallinity, an earlier crystallization (beginning at higher temperatures) and a shorter half-time of crystallization.

The crystallization rate depends not only on the thermooxidation reaction of the components but also on the thermo-mechanical degradation processes. The repeated processing generated shear forces which induced chain scission of the polymer. During reprocessing, the shorter polymer chains were probably formed as a consequence of chain scission. According to the kinetic theory of polymer crystallization [32], the lamellar growth controlled by the process of coherent two-dimensional surface nucleation depends on the lateral surface energy and fold surface energy of a crystal. According to Godovsky and Slominski [33], the difference in the nucleation ability of polypropylene may be connected with the morphology of the polymer crystallized from the melt. They concluded that kinetic parameters are related to changes from athermal to thermal nucleation, and initiation of the secondary crystallization process. On the other hand, the crystallization parameters strongly depend on the molecular weight of polypropylene. Reorganization (thickening) of the lamellae during crystallization is more pronounced with the number of processing cycles which may lead to shortening of the chains.

Additional investigations are needed to clarify the role of thermooxidation or thermo-mechanical degradation processes in nucleation activity. Thermal analyses (TGA or others) will be used to clarify it.

Moreover, based on the theory of heterogeneous nucleation, the interfacial free energy function will be determined as well as the supermolecular structure of semicrystalline components of the blends will be investigated using PLM (Polarized Light Microscopy) and SEM methods.

CONCLUSIONS

The results obtained in this study allowed to draw the following conclusions:

— Significant changes of the crystallization peak temperature T_{cp} of polypropylene matrix in multirecycled PP/PA6 blends were observed. An increase in T_{cp} of PP by about 12 °C was noted in the blends before reprocessing in comparison with pure PP. For the blends recycled 2–8 times, the T_{cp} values of PP remained practically unchanged. However, further reprocessing (tenth time) induced significant changes in the T_{cp} value (shift of DSC exothermic peak towards higher temperature by ca. 5 °C).

— The extent of crystallization of polypropylene in the blends was significantly higher than in pure PP and decreased with the number of reprocessing cycles.

— The half-time of PP crystallization in PP/PA6 blends was shorter than that for pure PP. This parameter decreased with the number of reprocessing cycles. From the above results it can be concluded that repeated extrusion of PP/PA6 blends acts like nucleating process for PP.

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