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Isothermal Crystallization Kinetics of Poly (Ethylene Terephthalate) – Cellulose Acetate Blends

Yogaraj U. Nabar, Ajay Gupta, Ramani Narayan (✉)

Department of Chemical Engineering & Materials Science, 2527 EB, Michigan State University, East Lansing, MI-48824
E-mail: narayan@msu.edu; Fax: 517-432-3563

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Summary

The isothermal crystallization exotherm was determined at three temperatures for two blends of bottle regrind Poly(ethylene terephthalate) (PET) with Cellulose Acetate (CA) as derived by an extrusion process, as well as for the pristine PET. It was observed that the addition of 10 weight-percent CA increased the crystallization rate of PET manifold, which resulted in improved moldability with faster cycle times. The crystallization was observed to be very fast with initiation times of the order of a few seconds, perhaps due to the impurities present in the bottle regrind PET and the synergistic effects of the CA particles. The fast rate of crystallization and high melting point of PET (250°C), and the degradation of CA at temperatures higher than 260°C made extrusion of PET – CA blends difficult. However, increasing the CA content in the blend to 30% decreased the rate of crystallization of PET resulting in an improved extrusion process, but slower cycle times.

Introduction

Twin-screw extruders (TSEs) have been widely used in the polymer industry to make polymer blends. The performance of a polymer blend depends on the properties of its component polymers, and the final blend morphology. One of the major parameters is the crystallinity, which dictates the mechanical and thermal properties and the processing conditions of the polymers and their blends with other polymers and fillers [1 – 15]. In a polymer blend, both the components may be crystalline, or one may be crystalline and the other amorphous. In addition, the blends may be miscible or immiscible. In the case of immiscible blends, if there is a large difference in melting points of the polymers, the component with the higher melting point will crystallize in the molten phase of the other component, which will affect the crystallization process through the effect of its viscosity on the mobility of the crystallizing polymer chains. On the other hand, the lower melting polymer will crystallize in the presence of the solidified particles of the other component, which may act as nucleating agents.

In the case of miscible blends, the presence of a single T_g widens or narrows the temperature range of crystallization of the constituent polymers. If the T_g shifts nearer to the melting point of the polymer, both the degree and rate are seen to be reduced.

The molecules of the crystallizing polymer may be hindered by those of the second component, and in some cases, co-crystallinity is observed. In such co-crystalline blends, the components are mixed in the crystalline as well as the amorphous regions, for instance, a blend of low-density polyethylene (LDPE) with a copolymer of ethylene, propylene and 1, 4-hexadiene [6].

Due to the interplay of these factors, the morphology of a blend is more sensitive to the processing conditions, and this can be utilized effectively to obtain a broader range of property combinations from a single blend composition.

PET is a semi-crystalline polymer with a melting point of about 250°C. The crystallization of PET in blends with other polymers has been widely studied due to its commercial importance. The main property improvements sought are improved moldability with faster mold cycles, less warping and high heat distortion temperature. It is of increasing interest nowadays to utilize recycled PET, which is less expensive as compared to virgin PET, and has to be put to a lower grade use due to impurities. However, whatever the lower grade use, the recycled PET needs to be blended with a high melt-strength polymer to obtain satisfactory mechanical properties for the recycled PET.

Natural polymers such as starch, cellulose, and their derivatives such as starch and cellulose acetates, cellulose propionate, etc. are being increasingly sought as a replacement (partially or in full) for synthetic polymers derived from petroleum [16, 17]. Moreover, these polymers have the advantage that they are chemically or biologically degradable, and thus can be recycled back to earth instead of being reused in low-grade applications. Cellulose Acetate (CA), having high melt-strength, is a derivative of the natural polymer cellulose in which some of the hydroxyl groups are replaced with acetate groups to reduce the hydrogen bonding, and make the polymer easier to process [18]. It is known that the biodegradability of CA depends on the degree of substitution (DS) ($0 \leq DS \leq 3$). This biodegradation can be observed in samples which have a DS < 2.5 [19]; CA with a DS of 2 is used in this study.

It is desirable to keep the processing temperatures as low as possible to minimize degradation of CA and due to low melt strength of PET. The extrusion of PET-CA blends was found difficult as the PET crystallized and clogged up the die and the barrel of the extruder. If the extrusion temperature was kept higher, it would degrade the CA and the blend was unacceptably discolored. Therefore, crystallization studies were undertaken to better understand and possibly solve the problem. In this paper, we report on the crystallization of PET-CA blends obtained by extrusion processing, and compare to that of the bottle regrind PET.

Experimental

Materials

Poly(ethylene terephthalate) used for these experiments was ‘bottle regrind’ of weight-average molecular weight, $M_w \sim 40{,}000$, a T_g of 78°C, and a melting temperature of 249°C as supplied by Hoechst Celanese, Charlotte, North Carolina. Cellulose Acetate (grade JLF-68) supplied by Hoechst Celanese had a M_w of $\sim 55{,}100$, an M_n of $\sim 11{,}800$, T_g of 191°C, and a melting temperature of 230°C. The melting endotherm started at 218°C.

Experimental Setup

The experimental setup used in the blending of CA with the PET was a twin-screw extrusion system. The twin-screw extrusion system consisted of an extruder driver with a speed control gearbox, a Werner Pfleiderer ZSK-30 twin-screw co-rotating extruder with a screw diameter of 30 mm, an L/D of 32, accurate single-screw feeders for feeding CA and PET respectively. The screw configuration, comprising of alternate conveying and kneading zones, was employed in the extrusion of the PET-CA blends and is shown in Figure 1.

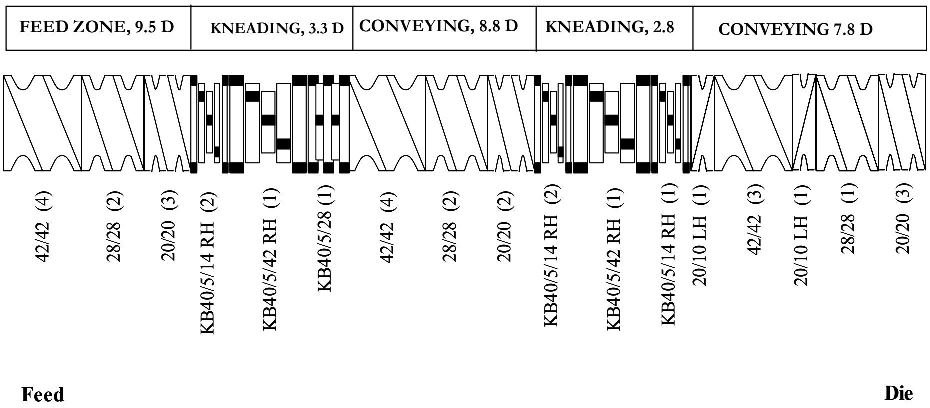

Figure 1. Screw Configuration for the Extrusion of PET-CA blends.

A cylindrical filament die 3.2 mm in diameter and 9.6 mm in length, with a cooling sleeve was assembled to the extruder. The die could be easily removed and was not used whenever there was too much die-swell or when the material in the die resulted in unacceptable degradation. The barrel could be cooled by adjusting the flow rate of the cooling water supply, which was manually controlled using valves for each of the six heated zones. The sensors were mounted on the die to measure the temperature and pressure of the melt.

Procedure

The CA, PET and the blends obtained by extrusion were always dried before extrusion or injection molding to minimize degradation of the material. Improper drying of the feed also resulted in poor injection molded samples. The materials were dried in a convective oven at 70°C for at least 8 hours before processing.

The temperatures in the extruder zones were set up to reach the required temperatures for the melt blending of CA with PET. The temperature profile during extrusion was 20/190/220/240/250/245/225°C from the barrel section just after the feed throat to the die, with a melt temperature of 235°C -240°C. Blends of 90% PET / 10% CA and 70% PET / 30% CA (by weight) were prepared in the twin-screw extruder.

Characterization

Differential Scanning Calorimetry (DSC)

Isothermal crystallization studies were carried out using a modulated DSC 2920 from TA Instruments on 20 mg samples of extrudates and bottle regrind PET in a closed DSC pan under nitrogen flow.

Results and Discussion

Figures 2-4 shows the isothermal crystallization kinetics of pure bottle regrind PET, 90% PET-10% CA, and 70% PET-30% CA recorded at 200, 210 and 220°C. The temperature of the samples was raised to 290°C, and held there isothermal for 2 minutes to ensure that all the crystallites melted. The temperature was then brought down at a cooling rate of 130°C/min to the desired temperature and held isothermal for 30 minutes, i.e. a time long enough to reach the complete crystallization of samples. It is worth noting that due to the high rate of crystallization and the short induction time, crystallization at temperatures less than 200°C could not be studied with this technique. Even with this rapid rate of cooling (130°C/min), the initial crystallization exotherms could not be recorded in all the experiments (see Figures 2 – 4). It seemed that the induction time for the onset of crystallization was of the order of a few seconds. Ahroni [8] has reported an induction time of 10 seconds for PET. It is worth noting that Brucato et al. [7] have reported cooling rates of up to 400°C/sec by using thin samples of polymer (nucleated polyamide 6) in a copper die equipped with a thermocouple.

The total time for crystallization for PET homo-polymer at 200°C was 4 minutes. Comparing this with the data of Kim et al. [20], who reported a total time for crystallization of about 30 minutes for PET of $M_w \sim 40,000$, it may be concluded, that this was either due to different thermal histories, or there could be some impurities present in the bottle regrind, which could have acted as nucleating agents. From Figures 2-4, the rate of crystallization was reported on Table 1, in terms of the "characteristic time" (T'), defined as the time taken for the crystallization to complete after the maxima in the crystallization exotherm was observed. It should be noted that the total time for crystallization was less than twice the T', because the crystallization exotherm was not symmetric. The time taken to reach the maxima was observed to be generally less than the time taken from the maxima to completion. After the crystallization was complete within a few minutes, the melting enthalpy of samples was also recorded by reducing the temperature of the samples to 160°C, and then again raising to 290°C at 20°C/minute. This was done to obtain a better baseline.

It is seen (from Table 1) that there was a large increase in the rate of crystallization for the blend containing 10% Cellulose Acetate. The CA phase seemed to aid in crystallization, perhaps by offering sites for nucleation. These results were similar to the findings of Shingankuli et al. [9], where the rate of crystallization of PET was enhanced by the addition of poly(phenylene sulfide) (PPS), indicating enhanced nucleation due to the presence of solidified PPS. Also, Escala and Stein [10] reported a miscible blend of PET-PBT. The T_g of PET is lowered resulting in an increase in crystallization rate of PET and a corresponding decrease in the crystallinity for poly(butylenes terephthalate) (PBT). Nadkarni and Jog [11] studied an immiscible blend of PET-PMMA. PET in the blend exhibited a low degree of crystallinity, although the rate of crystallization was increased.

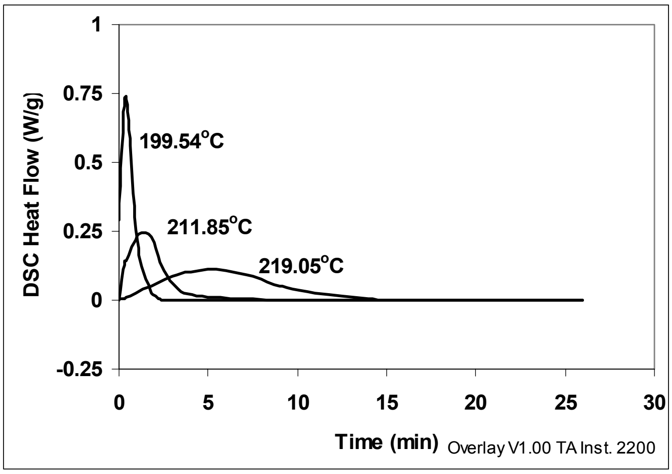

Figure 2. Crystallization Exotherms of Pure PET.

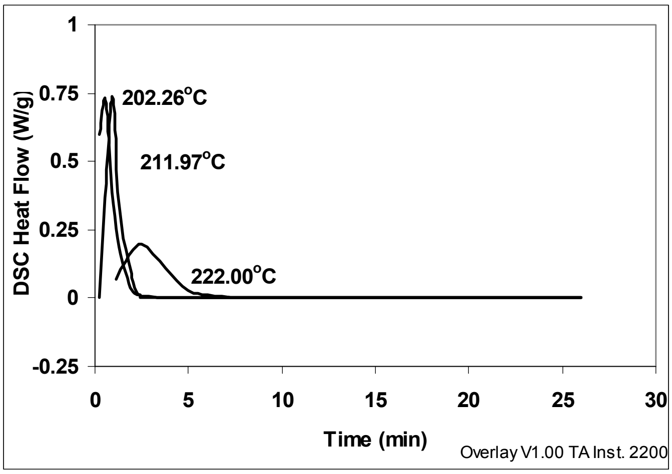

Figure 3. Crystallization Exotherms of 90% PET / 10% CA blend.

This was unlike the blends of PET with polyolefins in which the rate was reduced. Wilfong et al. [12] studied blends of PET and polyolefins (LLDPE, HDPE, PP, etc.). In these, the crystallization of PET took place in the melt of the other polymer and the rate of crystallization is reduced.

However, when 30% CA was used in the blend with PET, the rates of crystallization for the blends did not change significantly at 210°C and 220°C.

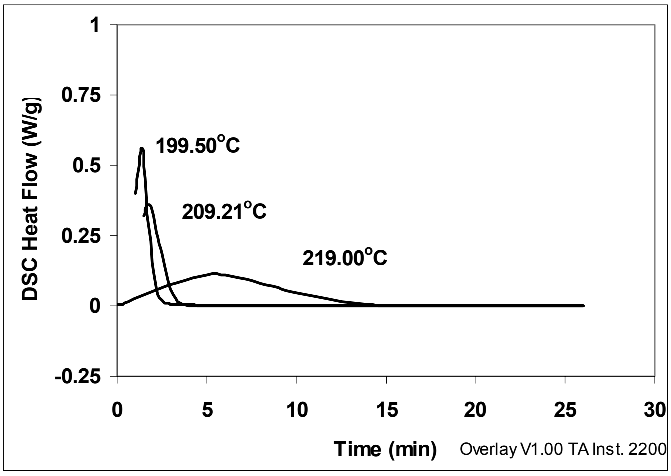

Figure 4. Crystallization Exotherms of 70% PET / 30% CA blend.

Table 1. Induction Times, Melting Enthalpies and Temperatures for bottle regrind PET and its blends with CA.

Blend	Temp (°C)	T' (seconds)	H_m (J/g)	T_m (°C)
PET bottle	200	128	50.98	250.33
regrind	210	184	52.68	249.01
	220	1218	51.43	248.58
10% CA	200	92	42.48	251.57
	210	111	47.41	247.44
	220	151	44.69	250.78
30% CA	200	90	32.85	252.62
	210	156	35.74	246.58
	220	1252	31.67	244.70

As shown by Figures 5 and 6, this may be due to the fact that the CA particles were agglomerating, reducing the effective number of nucleation sites, and also obstructing the molecules of PET. Above 218°C (start of the melting endotherm of CA), at 220°C, the rate of crystallization was almost the same as that for bottle regrind PET. In this case, the accelerating effect of nucleation sites was being offset by the retardation of PET chains by the melt of CA. Partially or completely miscible blends that have been studied are PET-PC [13 – 15]. All of them exhibited a slower crystallization rate and a lower degree of crystallinity of PET in the blend due to an increase in the T_g of PET. The effect of inorganic nucleating agents on the crystallization of PET has also been investigated [15].

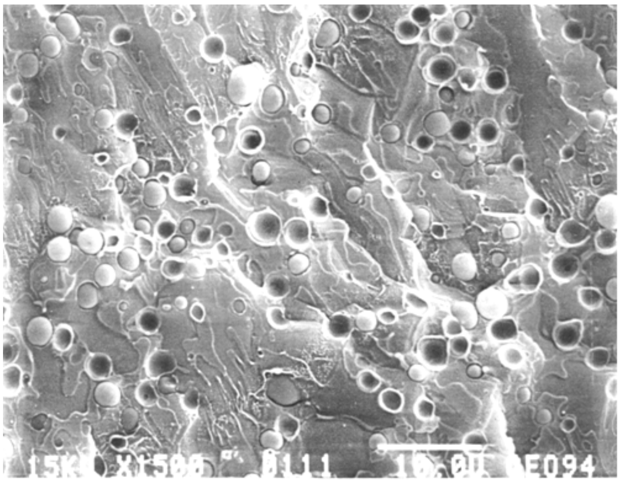

Figure 5. Scanning Electron Micrograph of 90% PET / 10% CA blend; sectioning perpendicular to flow, X 1500.

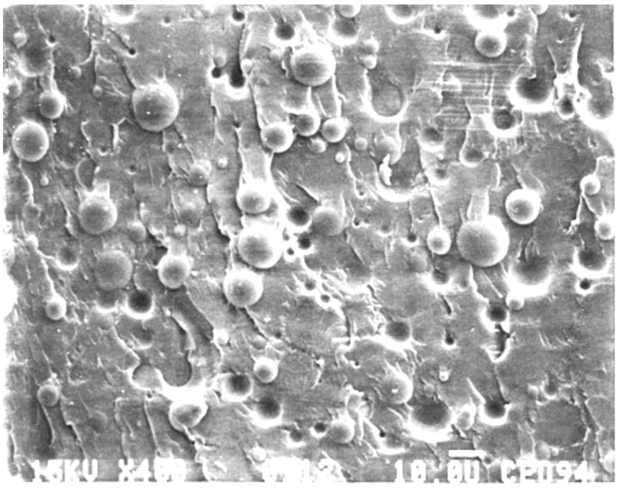

Figure 6. Scanning Electron Micrograph of 70% PET / 30% CA blend; sectioning perpendicular to flow, X 400.

It is worth noting that the samples heated to 290°C in the first heating cycle of the DSC did not show any obvious signs of thermal degradation of CA. If the CA would have undergone any thermal degradation in the heating cycle; the crystallization rate would have increased due to the degraded (burnt) particles. In such a situation, the blend involving 30% CA would have exhibited an increased rate of crystallization compared to the blend containing 10% CA, due to a higher amount of degraded material. The results obtained, however, indicated similar crystallization rates with the addition of 30% CA. Thus, it could be safely assumed that no significant degradation of the CA phase occurred during the heating cycle.

Figure 7 shows the enthalpy of melting (or crystallization under the isothermal conditions) plotted as a function of CA percentage.

A reduction in the extent of crystallization of PET was seen. Again for 10% CA at 210°C there was a slight increase in the extent of crystallinity. The crystallization of CA was suppressed, or it may be that the endotherm due to CA was not observed due to the closeness of melting temperatures of the two phases, in which case the decrease in the extent of crystallization of PET was offset by the crystallization of CA.

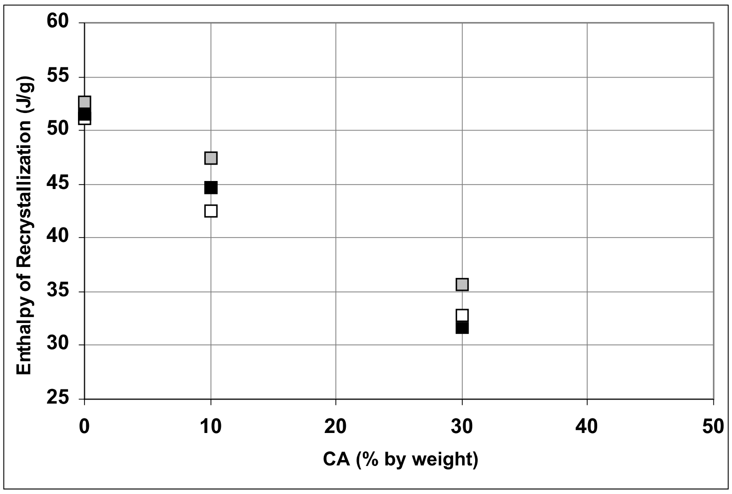

Figure 7. Enthalpy of re-crystallization of CA / PET blends: '□'– 200°C, '▨'– 210°C, '■'– 220°C.

Conclusion

To extrude blends of bottle regrind PET and CA, it was desirable to have temperatures as low as possible to prevent the degradation of CA and also because of the low melt strength of PET. However, due to the fast rates of crystallization, cold spots in the die and the barrel of the processing equipment should be avoided. It was observed that the addition of 10% CA increased the rate of crystallization of PET manifold, which resulted in improved moldability with faster cycle times. The crystallization was observed to be very fast with initiation times of the order of a few seconds, perhaps due to the impurities present in the bottle regrind PET and the synergistic effects of the CA particles. The fast rate of crystallization and high melting point of PET (250°C), and the degradation of CA at temperatures higher than 260°C made extrusion of PET – CA blends difficult. To prevent crystallization and degradation, the residence time should be reduced, perhaps by reducing the length of the die. This would also prevent the crystallization of PET due to elongation. Such crystallization due to orientation of the molecules has been reported by Van der Vegt et al. [21]. However, increasing the CA content in the blend to 30% decreased the rate of crystallization of PET resulting in an improved extrusion process, but a slower cycle times. Extrusion of blends with high CA content would provide melt strength and aid in the flow of dispersed PET, which has crystallized.

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