Heterogeneous Nucleation of Nylon 6 and PET with Selected Inorganic Compounds

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ABSTRACT: The effect of several inorganic compounds in the heterogeneous nucleation of poly(ethylene terephthalate) (PET) and poly(caprolactam) (nylon 6) was studied. Six inorganic chemicals were specifically selected, on the basis of their crystal structure, basal lattice dimensions, and thermal properties, in order to study the effect of temperature in their nucleation capabilities. Considering that temperature is one of the most important variables involved during processing of thermoplastics, the impact of the nucleation ability of the intentionally added heterogeneities was studied in terms of thermal conductivity, thermal expansion, and heat capacity. Six inorganic chemicals, which crystallize in the cubic system, were selected considering that they had variations in one of the thermal properties while the others remained practically constant along the temperature range of interest. The results indicated that, at constant surface area, chemical compounds with lower overall values of thermal expansion and also those with overall higher values of heat capacity promote heterogeneous nucleation; the effect of heat capacity was, however, also found potentially related to a different intrinsic mechanism. The impact of thermal conductivity was not considered significant. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 360–368, 2003

Key words: nylon 6 nucleation; PET nucleation; inorganic nucleating agents

INTRODUCTION

Poly(ethylene terephthalate) (PET) and poly(caprolactam) (nylon 6) are two important engineering thermoplastic semicrystalline polymers. Some applications of PET include carbonated soft-drink containers, packaging for food, X-ray films, magnetic tapes, and fibers for textile applications. Nylon 6, on the other hand, is mainly used for fibers, tire cord, and automotive part replacements (under-the-hood). Nucleating agents are heterogeneities resulting from mass impurities or purposely added additives in order to promote an increase in nucleation density in crystallizable polymers and enhance useful engineering properties. An increase in nucleation density often results in higher crystallinity, bending and tensile modulus, lower elongation at break and impact strength, reduced water absorption, and higher transparency. The presence of nucleating agents also has a favorable effect in the induction time for crystallization, shortening in practice the crystallization temperature, and as a consequence the cooling time during processing. Typical characteristics of heterogeneous nucleating agents include wetting or absorption by the polymer, high melting temperatures, and homogeneous dispersion. Insolubility is another characteristic, although some nucleants have also been reported to dissolve in and chemically react with the polymer.[1]

There have been several hypotheses on the mechanisms of action of nucleating agents; however, only three of these have been experimentally proved. The first and most important is called "epitaxial matching" and is of a physical nature.[2] Epitaxy has, however, been somehow controversial since it can be common to different polymers and crystalline structures[3–5]; nevertheless, there has been a considerable body of evidence that sustains this hypothesis.[6] Epitaxial nucleation has been experimentally observed in crystallization of flexible macromolecules such as polyethylene nucleating on NaCl (Ref. 7) and in crystallization of semirigid structures such as Nylon 6 nucleating on KCl.[8] A second mechanism, named "self-seeding," considers nucleation on crystal remains due to partial melting of primary crystals, and has also been observed with polyethylene.[9] A third and relatively new mechanism has been proposed, particularly for semirigid macromolecules chemically reacting with organic chemicals, an example being PET chemically nucleated with sodium 2-chloro benzoate.[10]

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Several inorganic compounds have been reported to physically nucleate nylon 6. Some examples are metallic oxides such as TiO_2,[11] binary halogenated salts as LiBr, LiCl, and KCl,[12,13] and the metallic halides $ZnCl_2$, $CaCl_2$, and NaCl.[14] Most of these reports have, however, focused on determining the influence of the corresponding additives on the physical and mechanical properties of the polymeric matrix rather than in the nature of the nucleation process itself. One of the few studies that considered nucleation in terms of epitaxial matching of nylon 6 on KCl was made by Willems.[7] Even though nylon 6 is an important engineering polymer, there have not been recent reports on its nucleation behavior with low molecular weight additives. Some new studies, however, used plain[15] and functionalized polypropylene (PP)[16] to show that the nylon 6 spherulite size is greatly diminished when it is blended with these polymers. Some inorganic oxides have also been studied as physical nucleating agents of PET, i.e., TiO_2, CaO, MgO, $BaSO_4$, SiO_2, and Al_2O_3.[17] Epitaxial nucleation of this polymer has not, however, been reported. PET is a higher crystallinity thermoplastic compared to nylon 6; therefore, fewer attempts have been made on understanding its nucleation behavior. One the most recent reports involved however an inorganic oxide, $CaCO_3$, which was used to demonstrate the reduction of interspherulitic amorphous regions as an indication of nucleation enhancement.[18]

During processing, semicrystalline polymers are first melted and then forced to flow under pressure through cavities before being injected into a mold and quickly cooled to make them crystallize as rapidly as possible. As a consequence both, polymers and additives, suffer strong temperature changes particularly during the cooling step. The thermal changes are expected to affect the main thermal properties of polymer and additives. Therefore, the main purpose of this study was to determine correlations between the nucleation ability of specifically selected inorganic nucleants and their main thermal properties. This view assumes from the beginning that changes in the thermal properties of the corresponding polymer, if present, will be constant as long as the experimental conditions remain the same.

EXPERIMENTAL

Materials and sample preparation

All nucleating agents used in this study were first milled and then passed through a 400 sieve (38 μm particle average diameter). Thermal properties and surface area were then measured for the selected nucleating agents before finally introducing them into the polymeric matrix. PET from Eastman Kodak, USA, had a number-average molecular weight of 19, 278 g/g-mol and a weight average molecular weight of 50,517 g/g-mol. Nylon 6, from Nylon of Mexico SA, had a number-average molecular weight, without extractables, of 18,700 g/g-mol. Two layers of polymer were first prepared using mica sheets, and the potential nucleating agents, always in concentration 0.5% wt, were homogeneously spread onto one of the two layers. Both layers of polymer were then sandwiched and melted together at the corresponding polymer equilibrium melting temperature (280°C for PET and 260°C for nylon 6). Melting was carried in a constant flow of nitrogen of 1 lt/min and also constant periods of time of 3 min, after which samples were quickly contacted to cold surfaces. Portions of these samples were then used for the nucleation studies.

Thermal properties

Thermal expansion was measured with a thermomechanical analyzer (TMA) Perkin-Elmer 7 and a dilatometer placed inside the sample holder. The system heating rate was 10°C/min from room temperature to 280°C using a constant counterweight of 10 mN. Al_2O_3 was used as the reference and the coefficient of volumetric expansion was calculated with

$$\beta = \frac{\Delta y \pi d^2 \rho}{4(w_t)R} \tag{1}$$

where Δy is the difference between curves of the velocity of expansion, d is the counterweight diameter, ρ is the sample density, w_t is the sample weight, and R is the heating rate.

Thermal conductivity measurements were made in a differential scanning calorimeter (DSC) Perkin-Elmer 7 using the method developed by Khana et al.[19] In order to calculate thermal conductivity, quartz was used as the reference compound and samples were prepared with the same dimensions as the quartz reference using a hydraulic press. Thermal conductivity was then calculated as in Khana et al.[19] using

$$K_x = K_s^* \left(\frac{M_x}{M_s}\right)^2 \tag{2}$$

where K_x and K_s are the values of thermal conductivity of sample and reference respectively, M_x and M_s are the slopes of the corresponding melting endotherms.

Heat capacity measurements were also made in the DSC using the "relation method" proposed by O'Neill.[20] In this case, two isothermal baselines were necessary to interpolate another baseline in the scanning zone. A sample was then scanned and the ratio dH/dt vs t was registered. The signal displacement was assigned to the heat absorption by the sample in accordance with

$$\frac{dH}{dt} = mC_p \frac{dT_p}{dt} \quad (3)$$

where m is the amount of sample,C_p is the heat capacity, and dT_p/dt is the programmed increase of temperature. The same procedure was repeated with Saphire in order to obtain the relationship between heat capacities with respect to a reference value before determining the heat capacity of samples.

Physical adsorption experiments were made in an ASAP2010 (Micromeritics, Inc.) physical adsorption equipment. Samples were first treated under vacuum, and either nitrogen or krypton was used to obtain the corresponding adsorption and desorption isotherms. These were needed to calculate the sample surface area using the Brunauer, Emmett, and Teller (BET)[21] equation:

$$\frac{P}{v(P^0 - P)} = \frac{1}{v_m c} + \left(\frac{c-1}{v_m}\right)\frac{P}{P^0} \quad (4)$$

where v is the reduced volume at standard conditions of the adsorbed gas at pressure P and temperature T, and v_m is the volume of a monolayer required to calculate the surface area.

Thermal analyses and nucleation

A Perkin-Elmer differential scanning calorimeter (DSC)-7 working under nitrogen atmosphere was used to characterize the thermal behavior of all samples. In typical nucleation experiments, 8 mg of sample were heated to the corresponding equilibrium melting temperature during a constant period of time. Samples were then cooled at the linear rate of 10°C/min and the DSC trace was registered.

An Olympus polarized optical microscope (POM) was used to measure the nucleation efficiency. Thin films containing 0.5% of KCl were first melt (3 min) at the corresponding equilibrium melting temperatures of both polymers in a Mettler FP82HT hot-stage. Samples were quickly transferred to another hot-stage and the nucleation process was videotaped as a function of time. The nucleation density was then determined by counting the number of nuclei in a constant area of 0.0025 mm^2.

RESULTS AND DISCUSSION

Epitaxial matching and surface area

The mechanism of epitaxial polymer crystallization is associated with oriented overgrowth of a polymeric crystalline phase on the surface of another crystalline phase. In this form, nucleation involves a primary mismatch between the lattice distance of the substrate and the deposited polymer. As a consequence, the substrate acts not only as an "inert spacer element" but also as an inducer of crystalline arrangements that do not occur under ordinary circumstances. This mechanism can occur in the vapor phase, solution phase, and melt phase. However, the decreased mobility in the molten state, where the molecular degrees of freedom are greatly restricted, makes it more difficult to have the required conditions for epitaxial matching. In order to experimentally determine epitaxial nucleation, the mismatch percentage between substrate and polymer lattice distances must be within a range of 15%[2] and can be calculated through

$$\%\, m = C - C_o/C_o \quad (5)$$

where C and C_o are the involved lattice distances of polymer and substrate, respectively. In the present work, only cubic substrates were selected with the purpose to eliminate the effect of variations in unit cell lattice parameters of substrates. These systems in their basal form have a single unit cell dimension (d') which can experimentally be determined using the Debye–Scherrer method.[22] However, in accordance with Mauritz et al.,[2] it is better to consider the distance between consecutive atomic layers with the same charge, δ, as a possible distance for epitaxial matching. The two distances are related through

$$\delta = \frac{d'}{2^{0.5}} \quad (6)$$

The corresponding values of d' for the nucleating agents used in this work were previously reported (see, for example, ref. 22) and they are compared with the calculated δ values in Table I. The mismatch percentage of each of the chemicals selected, after a primary scrutiny among 50 inorganic compounds, is also shown. From here, it is observed that in their basal crystalline form and at least along the basal ⟨100⟩, ⟨010⟩, and ⟨001⟩ directions, none of the selected chemicals would favor epitaxial matching with neither PET nor nylon 6. This direct comparison is however oversimplified since any other correlation distance would also have to be considered. For example, using nylon 6, Fisher and Willems[23] determined a very close lattice mismatch between alternate chains and every fifth row of unicharged ions along the ⟨130⟩ direction on crystals of KCl (one of the chemicals selected in this work). Therefore, the number of potential mismatch distances is quite high and, as a consequence, it would become very difficult to totally discard this mechanism as the most probable in polymer nucleation. However, in support of our lattice mismatch calculations, and contrary to the previous reports on epitaxial nucleation of nylon 6 on KCl,[8] we did not observe nucleation effects of this compound on nylon 6 (see

TABLE I
Single Dimension of Unit Cell (d^1), Distance Between Files of Atoms with the Same Charge (δ), and Mismatch Percentage of the Inorganic Chemicals with Nylon 6 and PET

Cubic substrates	d^1 (Å) 20–22	δ (Å)	m% N6 (α)	m% N6 (γ)	m% PET
NiO	4.177	2.954	>15%	>15%	>15%
MgO	4.212	2.978	>15%	>15%	>15%
AgCl	5.550	3.924	>15%	>15%	>15%
KBr	6.580	4.653	>15%	>15%	>15%
CaF_2	5.460	3.861	>15%	>15%	>15%
KCl	6.293	4.450	>15%	>15%	>15%
CsBr	4.287	3.031	>15%	>15%	>15%

results later). Nevertheless, the purpose of this study was not to elucidate the molecular nature of the mechanism of action of the nucleating agents involved but rather to determine correlations between the most important thermal properties and the nucleation process itself.

The inorganic chemicals used in the present work were homogeneous in size, and they were all well dispersed before being sandwiched and melted together with the polymeric layers. Considering that the external surface of nucleating particles is what is finally in intimate contact with the polymer, their surface area was also measured. Table II shows the relationship between the selected inorganics and the measured surface area. From here, it is clear that this parameter was always at low levels, compared to typical porous materials, and within the range of 0.2–4 m^2/g. This is important because samples with low surface area have low porosity and, as a consequence, a higher probability of surface contact with the polymer.

Thermal conductivity

The inorganic chemicals used to analyze the effect of thermal conductivity were KBr and AgCl. These chemicals were selected due to variations in their thermal conductivity while their heat capacity and thermal expansion remained practically constant in the range of temperature between the melting and crystallization temperature of the respective polymers. The experimentally measured values of thermal conductivity, using the method of Khana et al.,[19] are shown in Figure 1. From here, it is observed that overall KBr has higher values of thermal conductivity than AgCl. KBr has been used as a substrate in epitaxial growth of different polyamides other than nylon 6, including nylon 7, nylon 8, nylon 6,6 and nylon 6,10.[8,24–26] AgCl has not been used on nucleation of neither PET nor nylon 6.

TABLE II
BET Surface Areas and Gas Used for Its Determination for the Indicated Nucleating Agents

Nitrogen	NiO 3.4 (m^2/gr)	MgO 32.3 (m^2/gr) 4.0[a]
Kripton	KBr 0.2	AgCl 0.2
	KCl	CsBr
Nitrogen	0.4	0.5

[a] Thermally treated at 1210°C, 2 h.

Figure 2 shows the DSC cooling traces of nylon 6 containing KBr and AgCl and Figure 3 the corresponding to PET. This typical method used to determine the nucleation effect assumes that purposely added heterogeneities will contribute with their surface to decrease the energy barrier toward nucleation, increasing as a consequence the overall crystallization temperature. Table III shows the evolution of crystallinity calculated from the DSC data. The unfilled as-received polymers are shown as a reference. Both KBr and AgCl had a similar low effect in the heterogeneous nucleation of nylon 6. In the case of KBr the exothermic peak was located at 187°C and in the case of AgCl at 185°C. It needs to be mentioned, however, that we systematically observed all our nucleation results with nylon 6 not as significant as with PET as an indication of the different nature of each polymer. Nevertheless, we kept the same method of introduc-

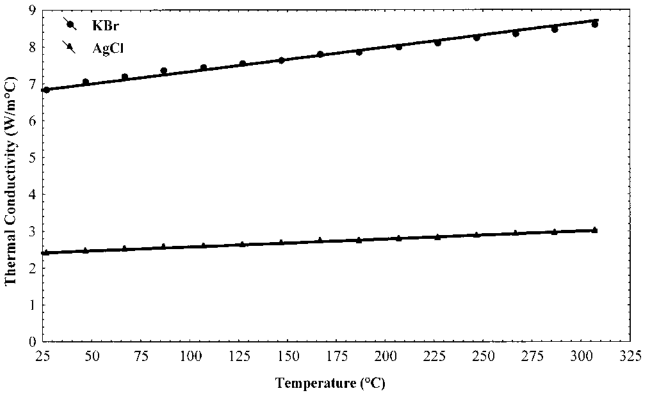

Figure 1 Thermal conductivity measurements of selected inorganic chemicals with constant heat capacity and thermal expansion and variable thermal conductivity.

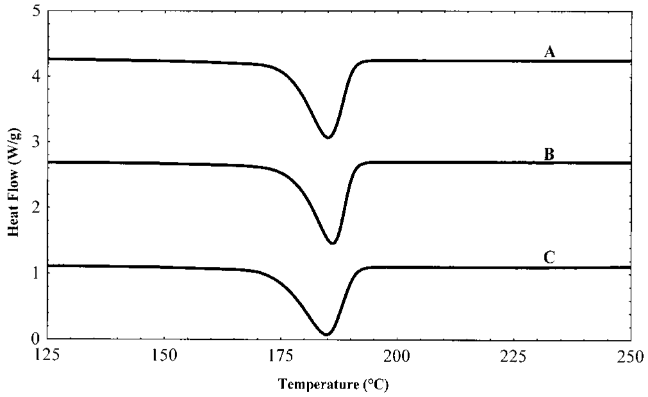

Figure 2 DSC cooling traces of nylon 6 with 0.5 wt % of inorganic compounds with variable thermal conductivity. (a) Nylon 6 and AgCl; (b) nylon 6 and KBr; and (c) nylon 6 without nucleating agent.

tion of the nucleating agent in PET in order to have a constant reference for both polymers. The change in crystallinity was imperceptible for nylon 6. The nucleation effect of KBr and AgCl on PET was about 25°C as shown in Figure 3. For KBr there was the exothermic crystallization peak at 196°C and for AgCl at 198°C. Crystallinity remained practically constant in this case, as shown in Table III.

In order to compare the effect of thermal conductivity and the other properties under study, another reference was also taken. This involved the change of the property with temperature (i.e., the slope of the corresponding experimental curve). For example, KBr presented a slope of 6.2×10^{-3} m °C^2/W and AgCl one of 2.2×10^{-3} m °C^2/W. In other words, even though there is a higher overall thermal conductivity and change of this property in KBr, the effect is not translated into the nucleation of either nylon 6 or PET. Therefore the previous results were taken as an indication of negligible influence of thermal conductivity in the heterogeneous nucleation of both polymers.

TABLE III
Crystallinity Results for PET and Nylon 6 Containing 0.5% wt of the Selected Inorganic Chemicals

	T_c (°C)	% X_c
Nylon 6[a] ΔH_c = 230 J/g		100
PET* ΔH_c = 140 J/g		100
PET + AgCl	198.7	34.9
PET + KBr	193.6	34.3
PET as-received	178.1	31.0
N6 + AgCl	184.9	29.6
N6 + KBr	186.0	29.6
N6 as-received	184.8	29.5
PET + CsBr	193.5	33.5
PET + KCl	202.0	34.7
N6 + CsBr	184.2	29.5
N6 + KCl	184.4	29.4
PET + MgO sintering (1210°C, 2h)	206.0	29.6
PET + NiO	193.5	31.7
N6 + MgO sintering (1210°C, 2 h)	187.0	25.7
N6 + NiO	185.0	30.8

[a] Wunderlich.[29]

Thermal expansion

Two inorganic chemicals were selected to analyze the effect of thermal expansion maintaining constant heat capacity, thermal conductivity, and surface area. These were KCl and CsBr. Figure 4 shows the experimentally measured dilatometric behavior as a function of temperature in the range of interest. KCl has been reported to promote epitaxial nucleation of nylon 6 thin films obtained from dilute solutions.[7,8] It has also been reported that KCl promotes the formation of the α form of nylon 6, decreasing also its melting temperature.[12] KCl has not, however, been studied as a nucleating agent of PET. Figures 5 and 6 show the DSC traces of nylon 6 and PET respectively after introducing KCl as nucleating agent. In agreement with these results, and particularly with PET, an inverse relationship between the nucleation ability and the overall values of thermal expansion which were lower

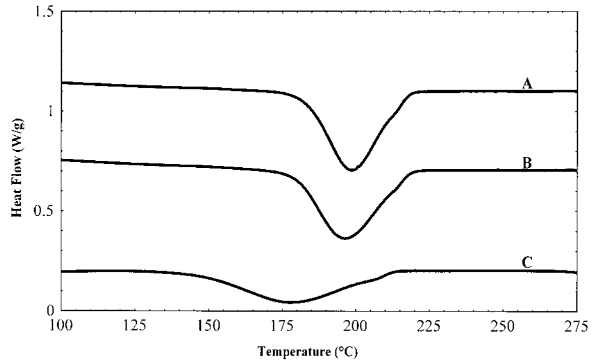

Figure 3 DSC cooling traces of PET containing 0.5 wt % of inorganic compounds with variable thermal conductivity. (a) PET and AgCl; (b) PET and KBr; and (c) PET without nucleating agent.

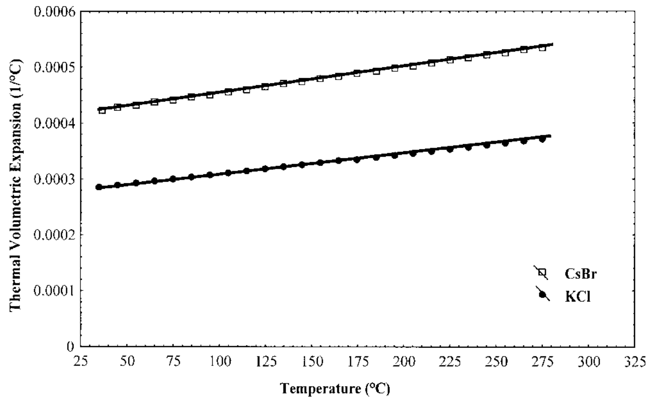

Figure 4 Experimental thermal expansion of inorganic chemicals with constant heat capacity and thermal conductivity.

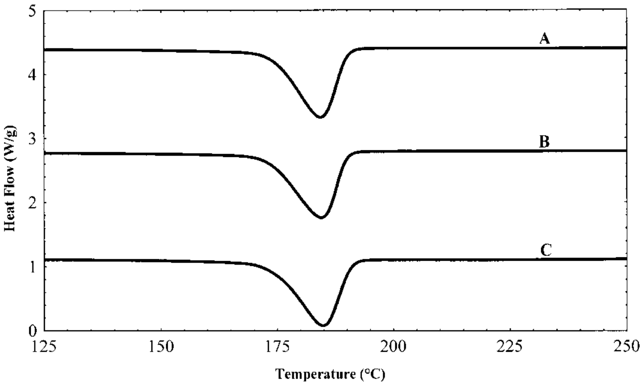

Figure 5 DSC cooling traces of nylon 6 with 0.5 wt % of inorganic compounds with variable thermal expansion. (a) Nylon 6 and CsBr; (b) nylon 6 and KCl; and (c) nylon 6 without nucleating agent.

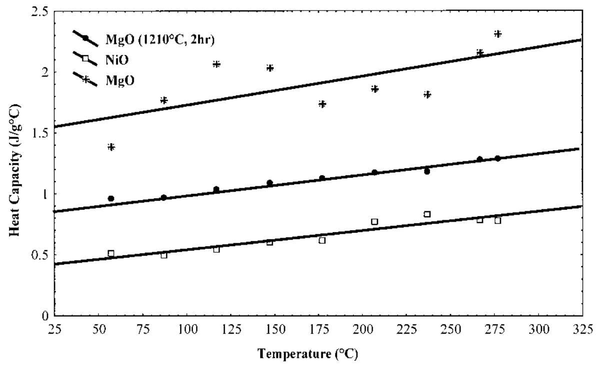

Figure 7 Experimental heat capacity of inorganic chemicals with constant thermal expansion and thermal conductivity.

for KCl than for CsBr (or also the change of thermal expansion with temperature: 3.6×10^{-7}°C^{-2}for KCl and 4.7×10^{-7}°C^{-2} for CsBr) is observed. In other words, an inorganic compound with low values of thermal expansion is more efficient in enhancing heterogeneous nucleation of both PET and nylon 6. A possible explanation for these results is that a higher amount of thermal expansion on heating the substrate, prior to nucleation, disturbs the polymer/substrate contact during the cooling stage, decreasing on average the possibility of heterogeneous contact. The PET crystallinity increased about 10% with KBr, as shown in Table III. As for nylon 6, the same effect was observed although in lower proportion and there was no important change in crystallinity.

Heat capacity

The third thermal variable studied in this work was heat capacity. Figure 7 shows the heat capacity measurements obtained for the two selected chemical compounds, MgO and NiO, for which thermal conductivity and thermal expansion remained approximately constant up to 300°C. In this particular case, sintering of the as-received MgO was necessary in order to have approximately the same values of surface area as those of NiO. Figures 8 and 9 and Table III show the corresponding DCS traces and crystallinity calculations after nucleation of both polymers. The local values of heat capacity were higher in MgO and the change of heat capacity with temperature was also slightly higher (1.7×10^{-3} Jg °C^2) than with NiO (1.5 $\times 10^{-3}$ Jg °C^2). If a correlation with these changes is considered, there would be a proportional behavior between heat capacity (or the change of this property with temperature) and the nucleation ability of the nucleating agent in PET. This is indeed observed in the DSC results of Figure 9. Interestingly, this is the only case where the results with nylon 6 are well defined, as shown in Figure 8. Therefore, it is clear that MgO is a nucleation promoter of both PET and nylon 6, motivating also an increase in crystallinity. The same behavior is observed with nylon 6 and in both cases there was an increase of crystallinity. These results can be considered an indication that the capacity to store energy works in favor of heterogeneous nu-

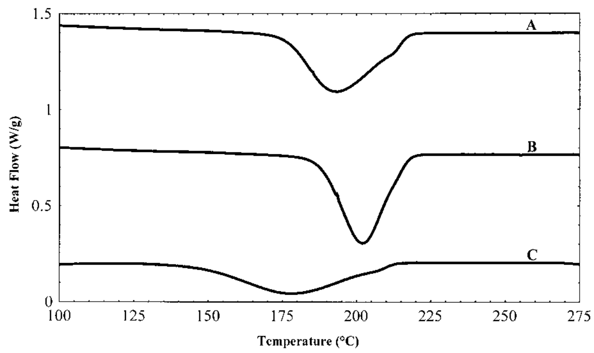

Figure 6 DSC cooling traces of PET containing 0.5 wt % of inorganic compounds with variable thermal expansion. (a) PET and CsBr; (b) PET and KCl; and (c) PET without nucleating agent.

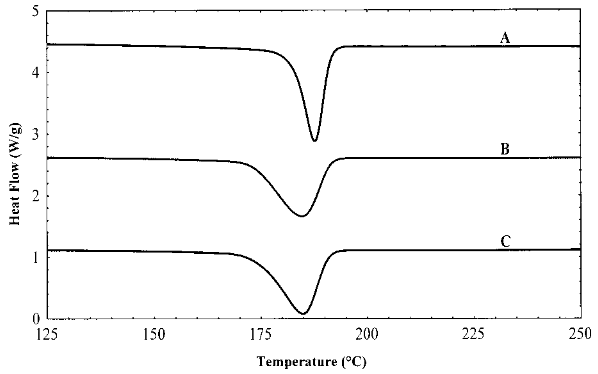

Figure 8 DSC cooling traces of nylon 6 with 0.5 wt % of inorganic compounds with variable heat capacity. (a) Nylon 6 and MgO; (b) nylon 6 and NiO; and (c) nylon 6 without nucleating agent.

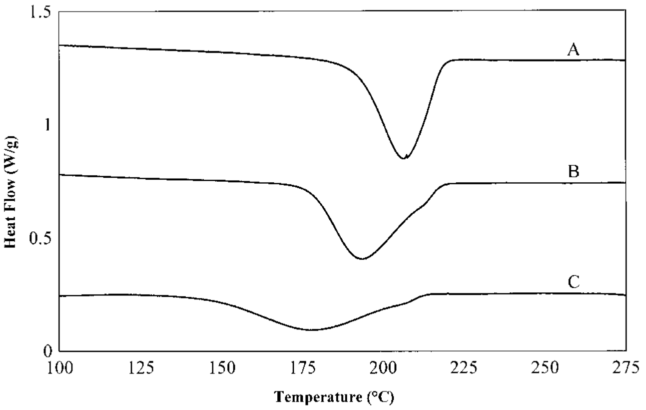

Figure 9 DSC cooling traces of PET containing 0.5 wt % of inorganic compounds with variable heat capacity. (a) PET and MgO; (b) PET and NiO; and (c) PET without nucleating agent.

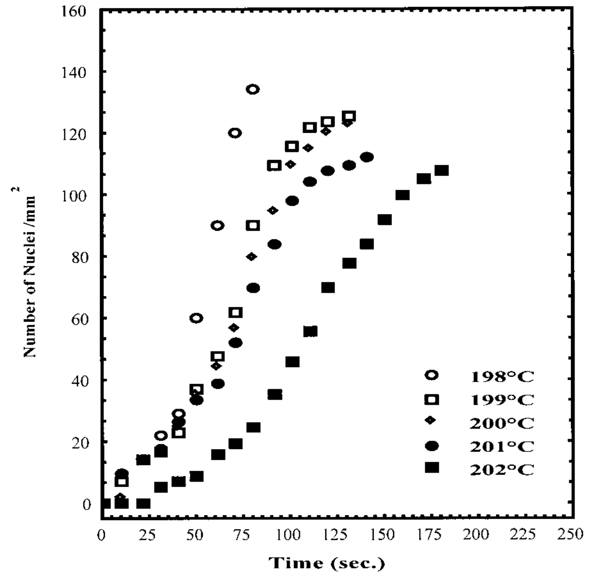

Figure 10 Nucleation isotherms of nylon 6 containing 0.5 wt % of KCl at different temperatures.

cleation. This is also in agreement with the opposite property, thermal conductivity, for which no effects were observed, as discussed before. A high heat capacity would then create a higher local temperature around the heterogeneities increasing as a consequence the probability of formation of heterogeneous nuclei. In this particular case, however, a correlation between the sintering process and the nucleation capacity has been observed; this could be an indication that the intrinsic nature of these nucleating agents is being modified with thermal treatment. This issue will, however, be addressed in a separate publication.[27]

Efficiency of nucleation

As discussed before, one of the most important nucleation effects observed in this study were those of thermal expansion. Therefore, the efficiency of nucleation was quantitatively determined for KCl, the purpose being to determine the general nucleation and crystallization characteristics of this potential nucleating agent. In order to determine the nucleation efficiency of KCl on nylon 6 and PET, the nucleation rate was measured in the range of temperatures 198–202°C for nylon 6 and 215–230°C for PET, and the results are shown in Figures 10 and 11, respectively. The experimental data were then correlated with[28]

$$\log I = \log I_o - \frac{\Delta F^*}{2.3kT} - \frac{16\sigma\sigma_e(\Delta\sigma)T_m^2}{2.3kT(\Delta T)^2(\Delta H_v)^2} \qquad (7)$$

The product $\sigma\sigma_e\Delta\sigma$ in eq. (7) can be obtained from the slope of the straight line given by $\log I$ vs $1/(T\Delta T)^2$. $T_m{}^{\circ}$ was 260°C for nylon 6 and 280°C for PET, k was 1.381×10^{-23} J/°K and ΔH_v was 2.16 erg/cm^3 for nylon 6 and 2.10 erg/cm^3 for PET.[29] Once the value of $\sigma\sigma_e\Delta\sigma$ was obtained, we used several reported values of $\sigma\sigma_e$ in order to obtain $\Delta\sigma$. Since $\Delta\sigma = \sigma + \sigma_c - \sigma_m$, then the efficiency of nucleation $(\sigma_m - \sigma_c)^{3-5}$ could be calculated. Table IV shows the results for nylon 6 and PET. Higher values of $(\sigma_m - \sigma_c)$ are indication of good efficiency of nucleation since a lower amount of energy is required to form the interface crystal–substrate.[3–5] Therefore, KCl can be considered an efficient nucleating agent for nylon 6. The efficiency of nucleation reported in Table IV once again indicates that KCl is also an effective nucleating agent for PET. The validity of these results is partly supported by the efficiency of nucleation of the neat polymers since it is

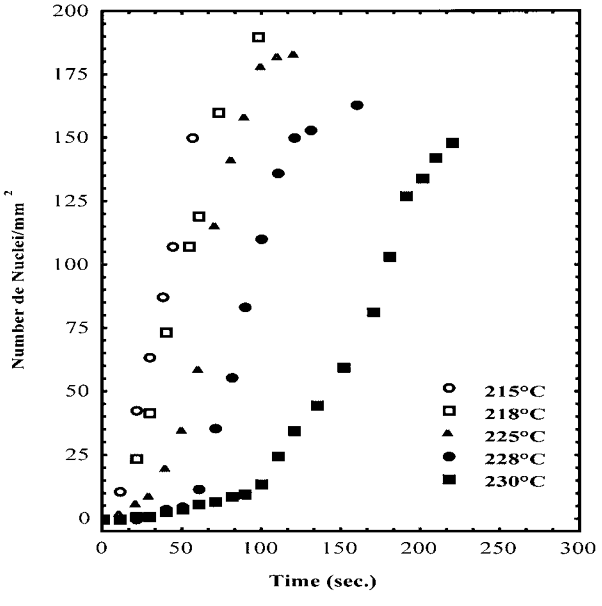

Figure 11 Nucleation isotherms of PET containing 0.5 wt % of KCl at different temperatures.

TABLE IV
Efficiency of Nucleation of Inorganic Chemical Compounds with Variable Thermal Expansion

Nucleating agent in nylon 6	$\sigma\sigma_e(\Delta\sigma)$ $(\mathrm{erg}^3/\mathrm{cm}^6)$	$\sigma\sigma_e$ $(\mathrm{erg}^2/\mathrm{cm}^4)$(a)	$\Delta\sigma = \sigma + \sigma_c - \sigma_m$ $(\mathrm{erg}/\mathrm{cm}^2)$	$(\sigma_m - \sigma_c)$ erg/cm^2, (assuming $\sigma = 8.0$ erg/cm^2)[a]
None	2355.7	480	4.9	3.0
KCl (0.5 wt %)	1702.5	480	3.5	4.4
Nucleating agent in PET	$\sigma\sigma_e$ $(\Delta\sigma)$ $(\mathrm{erg}^3/\mathrm{cm}^6)$	$\sigma\sigma_e$ $(\mathrm{erg}^2/\mathrm{cm}^4)$(b)	$\Delta\sigma = \sigma + \sigma_c - \sigma_m$ $(\mathrm{erg}/\mathrm{cm}^2)$	$(\sigma_m - \sigma_c)$ erg/cm^2, (assuming $\sigma = 19.3$ erg/cm^2)[b]
None	716.5	432	1.6	17.6
KCl (0.5 wt %)	337.7	432	0.7	18.5

[a] Magill.[30]
[b] Medellin-Rodríguez et al.[31]

well known that PET has a higher nucleation efficiency than nylon 6. However, the weakness of this method resides in the assumed values of σ. Therefore, it is incorrect to try to correlate the DSC results for both polymers since, for example, with nylon 6 there was a 40% nucleation enhancement that was not apparent in the DSC traces.

CONCLUSIONS

Several cubic inorganic chemical agents were used to study the influence of thermal properties in the heterogeneous nucleation of PET and nylon 6. These compounds were selected out of the conditions that involve epitaxial nucleation in order to concentrate the study on the main thermal properties of the nucleants. It was noticed, however, that totally discarding this last mechanism was difficult due to the high number of matching possibilities existing between polymer and substrate. Nevertheless, this did not influence the purpose of the present work. Considering that temperature is one of the main variables involved during processing of thermoplastics, the impact in the nucleation ability of the purposely added heterogeneities was studied in terms of thermal conductivity, thermal expansion, and heat capacity at low and constant surface area.

KBr and AgCl were selected to study the effect of thermal conductivity. and it was concluded that there is not a noticeable influence of thermal conductivity on the heterogeneous nucleation of both PET and nylon 6.

KCl and CsBr were used to study the effect of thermal expansion; both enhanced the effect, although an inverse influence of this property and the nucleation ability was found. Inorganics with low values of thermal expansion enhance better the heterogeneous nucleation of both PET and nylon 6. An argument to explain these results was that a higher amount of thermal expansion on heating the substrate prior to nucleation perturbates, on cooling, the polymer/substrate contact decreasing on average the possibility of formation of heterogeneous nuclei.

MgO and NiO were selected to study the influence of heat capacity; the results indicated that the capacity to store energy favors heterogeneous nucleation of both polymers. The effect may involve higher local temperature around the heterogeneity, increasing also molecular movements around it. As a consequence, the probability of formation of heterogeneous nuclei increases, the effect being more pronounced than that of thermal expansion. Here, however, there is also the possibility of having intrinsic effects associated with the nucleating agent itself.[27]

The KCl nucleation efficiency was measured in terms of the difference $(\sigma_m - \sigma_c)$; the results corroborated that, as indicated before, KCl is an efficient nucleating agent for PET and nylon 6.

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