Nucleation of PET Crystallization by Metal Hydroxides

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Synopsis

PET formulations containing small amounts of nonalkali metal hydroxides were prepared by extrusion from the melt. The efficiency of the hydroxides as nucleating agents was estimated from the elevation of T_{cc}, the crystallization temperature upon cooling from the melt, normalized for the purpose of comparison to a single convenient M_w (or the corresponding intrinsic viscosity). The results show that metal hydroxides capable of releasing water within the processing temperature interval of PET are effective nucleating agents for the crystallization of the polymer. Hydroxides releasing water out of said interval do not nucleate PET. There are two proposed nucleation mechanisms: (a) a localized severe hydrolysis of PET by the water released in the immediate neighborhood of the hydroxide particles and (b) a localized supercooling of the PET in the vicinity of the particles by the released water. The hydrolyzed PET of sharply reduced molecular weight has a T_{cc} significantly higher than the T_{cc} of the unhydrolyzed majority of the polymer. Upon cooling from the melt, and with the possible localized supercooling, the PET in the immediate vicinity of the hydroxide particles crystallizes first, nucleating the rest of the polymer. At present we can not verify whether both mechanisms operate concomitantly and which one of them is dominant.

INTRODUCTION

Presently there are several poly(ethylene terephthalate) (PET)-based, -reinforced, and -plasticized injection-molding formulations being introduced to the market. To be commercially viable, these formulations must crystallize in the mold upon cooling from the melt far more rapidly than pure PET. A method to achieve this rapid crystallization is through the elevation of the crystallization temperature upon cooling from the melt. This may be obtained by the incorporation of effective crystallization nucleating agents. A survey of the recent patent literature indicates an apparent concensus, according to which sodium salts of monomeric and polymeric carboxy acids are the most efficient nucleating agents for PET.

In a search for PET nucleating agents containing no alkali metals, we have found that certain metal hydroxides may serve this purpose admirably. In this report an attempt will be made to elucidate the nucleation mechanism for the crystallization of PET by metal hydroxides.

When one studies the thermal transitions of PET at a given cooling rate, one finds that the crystallization upon cooling from the melt or upon heating from the amorphous glass, at the temperatures T_{cc} and T_{ch}, respectively, is molecular-weight-dependent. T_{cc} increases with decrease in the molecular weight M, and T_{ch} decreases with a reduction in M. Due to minute amounts of impurities, residual polymerization catalysts, possible dust, and the fact that during processing and testing the samples are not at thermal equilibrium, exact reproducibility of T_{cc} and T_{ch} values is rather rare. However, when the experiment is repeated many times under identical conditions, the individual data points
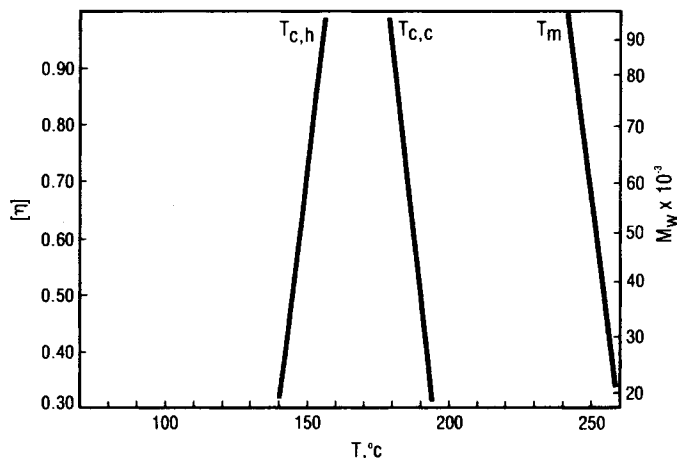
Fig. 1. Schematic first order transitions of PET as a function of M_w and $[\eta]$. Heating and cooling rates of 10 K/min and faster.

of T_{cc} tend to cluster more or less along a unique line. In the case of T_{ch} the data points cluster along another line of different slope. This is schematically shown in Figure 1. For a nucleating agent to be efficient, the T_{cc} line must be substantially displaced to higher temperatures and the T_{ch} to lower temperatures. The melting point, T_m, line is insensitive to the presence of nucleating agents in the bulk polymer, but shows about the same dependence on M or intrinsic viscosity $[\eta]$ as T_{cc}. The molecular weight dependence of T_{cc} and T_{ch} carries also to cases where nucleating agents are present. Therefore, in order to compare the efficiency of nucleating agents, the T_{cc} and T_{ch} values must be obtained from samples having the same molecular weight. Alternatively, one may normalize all T_{cc} and T_{ch} values to a single convenient molecular weight by translating experimental data points of various molecular weight samples, at the respective slopes of T_{cc} and T_{ch} master curves shown in Figure 1. It is important to recognize that for the purpose of comparing the nucleating efficiency of various agents, it is not the exact slope which is important but the consistent normalization of all pertinent data points along the same slope. A rapid way to estimate the molecular weight of PET is through its intrinsic viscosity ($[\eta]$ or IV) in a mixed phenol/tetrachloroethane solvent. An IV value convenient for normalization and, within the range of experimental results and usefulness, is IV = 0.50 dL/g. In the following, most crystallization results will be normalized, then, to $[\eta]$ = 0.50 dL/g, allowing for easy comparison of nucleating agents.

EXPERIMENTAL

The PET used for formulations studied in this work was an Allied Corporation product grade having an initial IV = 0.95 ± 0.02 dL/g. Occasionally an IV = 0.53 dL/g grade was used and in one instance grades of IV = 0.18 and IV = 0.08 dL/g were incorporated into formulations. In most cases the PET was ground before drying and mixing with other ingredients. The grinding of PET was performed at dry ice temperature in a Standard Model No. 3 Wiley Mill. In fewer instances

the PET was used in its "as-received" pelletized form. It was found that the reduction of water in the ground PET to an acceptable level required heating for 16 h or more in a vacuum oven operating at ≤0.3 mm Hg at temperatures of $125 \pm 5°C$. This temperature was insufficient for the PET in its pelletized form which required heating at $160 \pm 5°C$ under otherwise identical conditions. An acceptable level of resin dryness was one that upon extrusion resulted in a drop of IV by not more than 10% of its value before extrusion.

Additives to be studied for their nucleating capabilities were usually screened in their "as-received" powder form. Several of the more promising ones were finely ground with a mortar and pestel, or by tumbling in a ball-mill for 24 h. These additives were dried at $125 \pm 5°C$ or at higher temperatures in a vacuum oven as above for 16 h. For studies on the effect of predrying temperature on nucleation capability of aluminum hydroxide, occasional drying of $Al(OH)_3$ at temperatures higher than $300°C$ was conducted in muffle furnace. In these instances too, the drying times were 16 h. For routine preparations, the nucleating agents were added to the PET at a concentration of 1 wt %.

Compounding of additives into the PET was performed at temperatures above the T_m of the polyester. Stringent precautions were taken to avoid moisture pickup prior or during processing. The compounding was achieved in a Wayne 1-in. Single Screw Extruder having three zone heaters and a heated nozzle. Residence time of the molten mass in the extruder was usually maintained at about 3 min. The extrudate strand was cooled in water or a stream of dry air, pelletized, and dried prior to subsequent use.

Thermal data were obtained with a DuPont 990 Differential Scanning Calorimeter (DSC) instrument equipped with a DuPont Mechanical Cooling Accessory. In all DSC runs samples in argon atmosphere were heated from room temperature (RT) at a rate of 10K/min up to $300°C$. The samples were kept at $300°C$ for 5.0 min and then cooled to RT at 10K/min. Samples semicrystalline at RT were used to obtain T_m and T_{cc} values while samples melted and then quenched to be amorphous at RT were used to determine T_{ch}. In all cases the first-order transition temperature corresponded to the highest point of the respective DSC sharp peak. Thermogravimetric analysis (TGA) was conducted in an argon atmosphere using a DuPont 1090 TGA instrument and a heating rate of 10K/min. Wide angle X-ray diffraction (WAXD) patterns were obtained at RT with a Norelco diffractometer operating in parafocus geometry and using monochromatized copper K_α radiation. Scanning electron microscopy (SEM) was performed on specimens lightly shadowed with carbon to render their surface conductive. The instruments used were AMRAY 1600 SEM and JEOL JXA-50A electron probe microanalyzer.

The intrinsic viscosity of all specimens studied by DSC was measured at $25°C$ in internal dilution Cannon-Ubbelohde glass viscometers in a 60:40 wt/wt phenol/tetrachloroethane mixed solvent. Whenever desired, weight average molecular weights M_w were obtained from IV using the relationship[1]

$$[\eta] = 2.29 \times 10^{-4} M_w^{0.73} \tag{1}$$

GPC scans were obtained from solutions of PET in m-cresol with the Waters 150-C ALC/GPC instrument operating at $110 \pm 1°C$. In all cases exactly the same volume of 0.45% solution was injected to facilitate an easy comparison of the results by simple superimposition of the curves. Number average molecular

TABLE I
Metal Hydroxides as Nucleating Agents for PET[a]

Metal hydroxide	T_{cc} (°C)	IV of tested specimens	T_{cc} normalized to IV = 0.50 dL/g
Aluminum	215	0.54	217
Copper (II)	208	0.68	212
Nickel (II)	204	0.64	207
Indium	209	0.55	211
Barium	195	0.73	199
Magnesium	208	0.41	203
Cobalt (II)	206	0.44	203
Lanthanum	189	0.74	192
None (blank)	188	0.51	188

[a] All hydroxides at 1% concentration.

weight M_n was determined by end group analysis. Titrations for acid and amine end groups were performed in o-cresol. End group estimates were obtained by IR from the solid pulverized polymer with the results of titration and IR being in agreement within experimental error.

RESULTS AND DISCUSSION

Several metal hydroxides were chosen and compounded at 1% level into PET in order to determine their capability to nucleate the crystallization of the polymer. No alkali metal hydroxide was considered due to their strong hydrolytic degradation of the polyester. Typical results obtained with metal hydroxides are indicated in Table I. Nucleating agents increasing T_{cc} by at least 15K above the T_{cc} of the unnucleated blank were deemed to be effective. The rest were considered failures. Because it is colorless and inexpensive, aluminum hydroxide was chosen as the hydroxide to be investigated in detail.

To study the effect of the amount of nucleating agent, formulations were prepared as listed in Table II. As evident from this table, concentrations of aluminum hydroxide in the range of 0.75–1.5% are most efficient in raising the

TABLE II
Effect of Al(OH)$_3$ Concentration on IV and T_{cc} of PET

Sample code	Al(OH)$_3$ predried at 150°C[a]	IV	T_{cc} (°C)	T_{cc} normalized to IV = 0.50
-2B2	none	0.72	190	192
Batch IV	0.25%	0.70	195	202
Batch V	0.50%	0.68	197	205
-50A	0.75%	0.52	208	209
-50B	1.00%	0.54	215	217
-50C	1.50%	0.48	213	212
-50D	2.00%	0.45	213	211
Batch VIII	4.00%	0.31	217	212

[a] Predrying the aluminum hydroxide at 130°C or at 250°C yielded IV and T_{cc} results within the range of experimental scatter of the tabulated data.
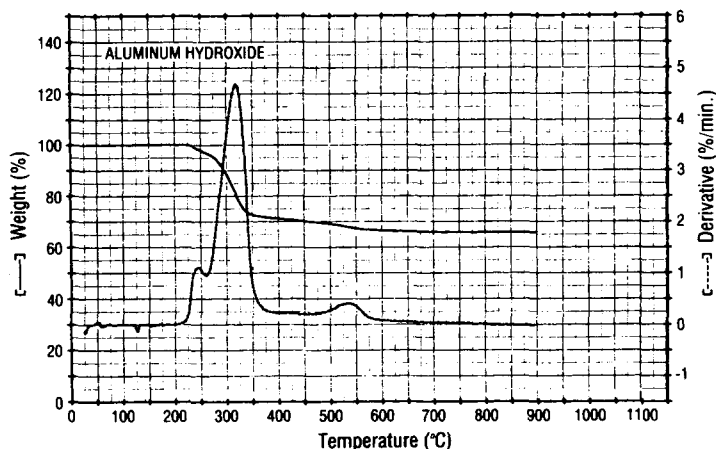
Fig. 2. TGA scans of aluminum hydroxide.

crystallization temperature T_{cc}. Predrying at 150°C or at 250°C caused no change in the nucleating efficiency of this agent. The reduction in T_{cc} for PET samples containing 1.5% and 2% aluminum hydroxide was found to be reproducible, as were all other tabulated results.

In an effort to elucidate the reasons responsible for the nucleating ability of the effective metal hydroxides in Table I, all the hydroxides in the table were subjected to thermogravimetric analysis. Typical results are shown in Figures 2–5. The TGA results indicate that in all cases where effective nucleators were scanned, they lost water over a narrow temperature interval spanning the processing temperature range of PET (260–300°C). On the other hand, in all cases where an inefficient nucleator was scanned, its TGA plot indicated water weight loss at temperatures too low below the PET processing temperature [e.g., $Ba(OH)_2 8H_2O$] or too high above the processing temperature [e.g., $La(OH)_3$ in Fig. 5].
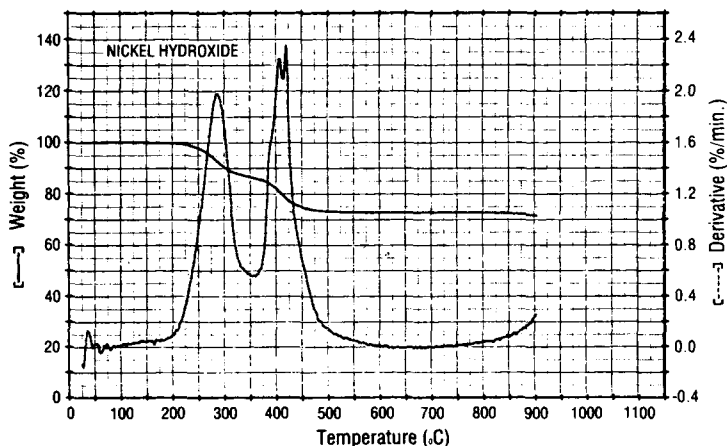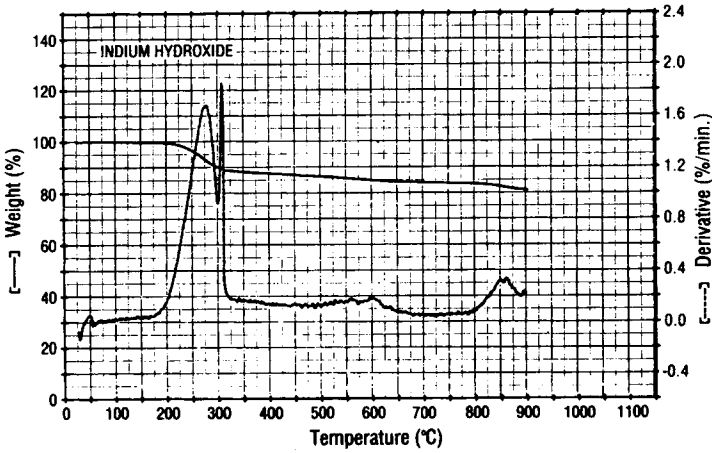

Fig. 3. TGA scans of nickel hydroxide.

Fig. 4. TGA scans of indium hydroxide.

The realization that a release of water by the nucleating agent into the melt during processing may be responsible for the efficiency of the agent led us to evaluate the efficiency of aluminum hydroxide predried at various temperatures ranging from 120°C up to 350°C. The results are tabulated in Table III.

The decrease in nucleation efficiency of Al(OH)₃ as a function of predrying temperature is graphically shown in Figure 6. The error bars show the range of data scatter obtained in repeated experiments. Returning to Figure 2, it becomes apparent that the lowered nucleation efficiency of Al(OH)₃ starting at predrying temperature of 250°C is associated with the onset of water loss at this temperature. The second sharp drop in nucleation efficiency, at predrying temperature of 350°C is associated with almost complete cessation of weight loss at these temperatures. TGA scans of aluminum hydroxide predried at 350°C reveal, a weight loss of about 8–9% spanning a temperature interval of 150° and centered at about 550°C, far above the processing temperature of PET. For
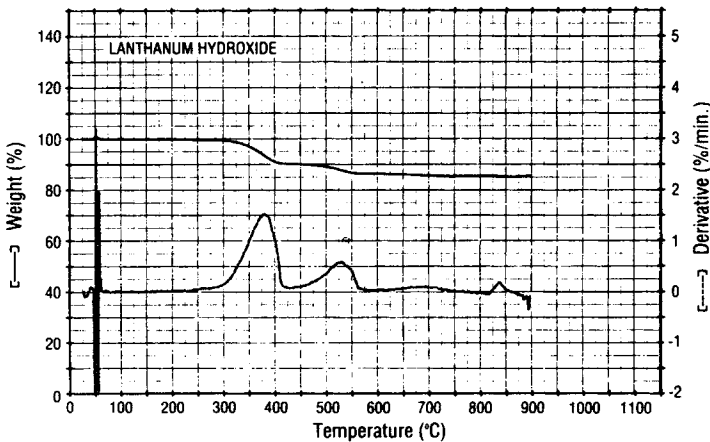

Fig. 5. TGA scans of lanthanum hydroxide.

TABLE III
Effect of Predrying Temperature of $Al(OH)_3$ on Its Ability to Nucleate the Crystallization of
PET[a]

Predrying temp (°C)	T_{cc} (°C)	IV of specimens	T_{cc} normalized to IV = 0.50 dL/g
120	219	0.45	218
130	215	0.54	216
150	216	0.51	216
250	212	0.58	213
270	209	0.55	210
280	203	0.56	204
310	202	0.60	204
325	203	0.50	203
350	190	0.72	194

[a] All at 1% $Al(OH)_3$ in PET formulation.

comparison several inefficient nucleating agents, including a few aluminas, are tabulated in Table IV.

WAXD patterns were obtained from aluminum hydroxide predried at 150°C, 250°C, 310°C, and 350°C. The aluminum hydroxide dried at 150°C (and routinely used for most formulations described in this paper) was identified as the mineral Gibbsite having the $Al(OH)_3$ formula and a $P2_1/n$ monoclinic crystal structure. The high temperature modification was identified as the mineral Bohemite having the AlOOH formula and C_{mcm} orthorhombic crystal structure. The samples dried at the intermediate temperatures contained varying amounts of the two extreme modifications. From the above a water loss in the interval 250–310°C is apparent:

$$Al(OH)_3 \rightarrow AlOOH + H_2O \tag{2}$$
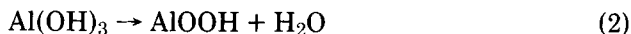
The weight of the lost water is about 23% of the $Al(OH)_3$. The TGA scan in Figure 2 indicates that in the 250–310°C interval about 27% of the samples weight
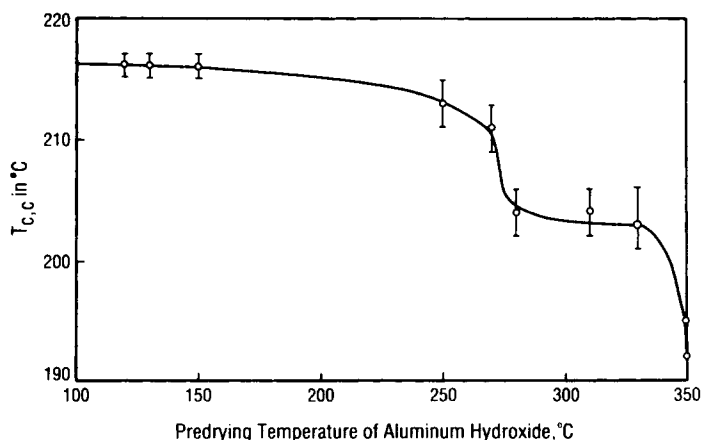

Fig. 6. T_{cc} of PET, IV = 0.50, as function of predrying of $Al(OH)_3$. 1% conc nucleating agent.

TABLE IV
Inefficient Nucleating Agents for PET[a]

Agent	T_{cc} (°C)	IV	T_{cc} normalized to IV = 0.50 dL/g
Fumed silica	190	0.53	191
$CaCO_3$	189	0.53	190
Alumina	194	0.68	197
Porocel alumina	196	0.79	201
F.M. active alumina	192	0.72	195

[a] All at 1% loading.

is lost. The difference of ~4% appears to be the 4% weight loss visible in the TGA scan in the temperature interval 235–270°C.

A PET formulation containing 4% $Al(OH)_3$ predried at 150°C was extruded and pelletized to obtain uniform dispersion. The intrinsic viscosity of the PET from the pellets was 0.31 dL/g and the T_{cc} of the pellets was 217°C. This corresponds to the expected T_{cc} of well-nucleated PET of such intrinsic viscosity. The pellets were dissolved in hot phenol/TCE solvent mixture and the aluminum hydroxide was filtered off. After washing twice with hot phenol/TCE and once with methanol, the solids were dried under high vacuum. WAXD patterns of the solids showed them to be a mixture of $Al(OH)_3$ and AlOOH. This indicates that a residence time of about 3 min close to 300°C is similar in its dehydrating effects on $Al(OH)_3$ to 16 h at 250°C.

SEM photographs were obtained from $Al(OH)_3$ samples dried at various temperatures from 130°C up to 350°C and from the aluminum hydroxide retrieved from the PET formulation described in the paragraph above. In all cases where the $Al(OH)_3$ was in the "as-received" powder form or was hand-ground, the morphology of the aluminum hydroxide appeared to be exactly the same. This morphological identity is surprising even though reported in the literature,[2] because WAXD indicated a transition of the samples from $Al(OH)_3$ to AlOOH.

Aluminum hydroxide finely pulverized in a ball mill appeared in the SEM as extremely fine featureless powder even under 3000X magnification. When incorporated into PET formulations, the amount of $Al(OH)_3$ required to initiate crystallization at a given T_{cc} was almost the same as the amount of "as-received" or hand-ground aluminum hydroxide. This is evident from comparison of Tables V and II. The somewhat lower nucleation efficiency of the finely pulverized $Al(OH)_3$ at the high loading levels of 2–4% will be commented on below.

SEM photographs were obtained from $In(OH)_3$ and $La(OH)_3$ dried at 150°C, and compared with photographs obtained from $Al(OH)_3$ at the same magnification. There was no morphological similarity between the three hydroxides. At best, the gross morphology of $La(OH)_3$ is closer to $Al(OH)_3$ than that of $In(OH)_3$. One recalls, from Table I, that the aluminum and indium hydroxides are effective nucleators while the lanthanum hydroxide is not. From the TGA scans in Figures 2, 4, and 5, one finds that $Al(OH)_3$ and $In(OH)_3$ release water in the processing interval of PET while $La(OH)_3$ releases water at temperatures significantly higher. This indicates that it is not the gross morphology of the

TABLE V
Nucleation Efficiency of Ball-Mill Pulverized Al(OH)$_3$

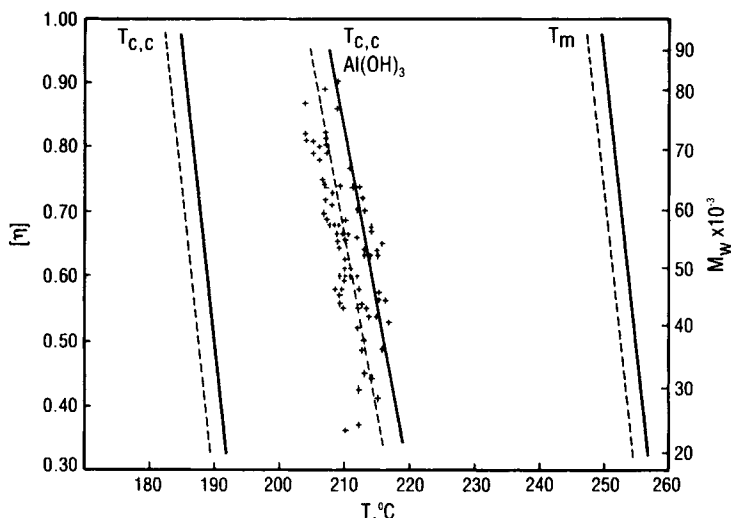| Sample code	Al(OH)$_3$ predried at 150°C	IV (dL/g)	T_{cc} (°C)	T_{cc} (°C) normalized to IV = 0.50	Sample code	Al(OH)$_3$ predried at 250°C	IV (dL/g)	T_{cc} (°C)	T_{cc} (°C) normalized to IV = 0.50
41A	Trace	0.79	193	198	32A	Trace	0.76	192	197
41B	0.10%	0.63	198	201	41G	0.10%	0.67	197	196
41C	0.25%	0.56	203	204	41H	0.25%	0.66	202	205
32C	0.50%	0.56	213	214	41J	0.50%	0.63	207	210
—	—	—	—	—	41K	0.75%	0.61	210	213
32D	1.00%	0.51	216	216	41L	1.00%	0.58	212	214
32E	2.00%	0.38	212	210					
32F	4.00%	0.33	211	208					

Fig. 7. Crystallization upon cooling from the melt, T_{cc}, and T_m of PET as a function of M_w or $[\eta]$: (—) transition temps of PET; (- - -) transition temps in PET containing 4–6% plasticizer. T_{cc} lines are for PET with no nucleating agents; T_{cc}–Al(OH)$_3$ lines are for PET containing 0.5–1.5% Al(OH)$_3$, Ni(OH)$_2$, In(OH)$_3$, Cu(OH)$_2$; T_m lines are for PET in presence or absence of nucleating agents.

hydroxide that controls its nucleating capability, but its ability to release some water into the cooling molten PET.

If one does not thoroughly dry pure PET prior to extrusion, the intrinsic viscosity and corresponding molecular weight of the extrudate will be drastically reduced. As shown by Schaul,[3] the percent loss of IV is linearly dependent on the amount of water present in the PET during extrusion. Batches of PET having initial IV of 0.95 dried under increasingly stringent conditions were extruded to obtain samples having IV ranging from IV = 0.5 up to IV = 0.95. Their T_{cc} values fall more or less on a line, as in Figure 7, at far lower temperatures than the T_{cc} values of hydroxide-nucleated PET of the same IV. When very large amounts of Al(OH)$_3$ were incorporated into the PET, the water released during processing caused sharp reduction in the IV of the resulting extrudate. We have noticed that, once the IV of the extrudate was reduced to $[\eta]$ <0.3 dL/g (from a starting value of IV = 0.95) then the T_{cc} values ceased to increase with reduction in IV and the T_{cc} normalized to IV = 0.50 actually started to decrease (cf. Tables II and V).

In a series of experiments, PET of IV = 0.95 was coextruded with amounts of PET of low IV, IV = 0.18 and IV = 0.08, with the amounts of the low-IV PET in the formulation increasing from 0% to 20%. The T_{cc} increased with the resulting decrease in IV of the extrudate, but in no case did it surpass the T_{cc} expected from pure PET of corresponding IV.

To check whether aluminum ions are effective nucleating agents for PET, the following compounds were formulated into PET in such quantities that the amount of introduced aluminum corresponded to 1% aluminum hydroxide: aluminum stearate, poly(ethylene-co-acrylic acid) (EAA) neutralized by aluminum ions, EAA neutralized by lanthanum, poly(ethylene oxide) complexed with Al^{+3}, and aluminum isopropoxide. None of these compounds was effective

TABLE VI
Comparison of Samples Hydrolyzed in Presence or Absence of Al(OH)$_3$

Sample code	Characteristics	IV	M_w	M_n	M_w/M_n
32	Blank; No Al(OH)$_3$	0.93	87700	58800	1.49
32FA	0.75% Al(OH)$_3$	0.66	54300	14500	3.74
32D	1.00% Al(OH)$_3$	0.51	38500	12700	3.03
32G	No Al(OH)$_3$; water hydrolyzed	0.53	40500	18500	2.19
32E	2.00% Al(OH)$_3$	0.38	25700	11500	2.23
32A	No Al(OH)$_3$; water hydrolyzed	0.38	25700	11900	2.16
32F	4.00% Al(OH)$_3$	0.33	21500	8200	2.62

in nucleating PET. We concluded, therefore, that aluminum ions do not nucleate PET.

The above indicated to us that it is neither the uniform presence of water throughout the sample nor the presence of aluminum ions in the system or the release of a large amount of water that are responsible for the nucleation capability of the effective hydroxides. To the contrary, it is the localized release of relatively small amounts of water into the cooling molten polymer that accelerates its crystallization.

It is our belief that two mechanisms possibly play a role in the nucleation of PET by aluminum and other effective hydroxides. Both are brought about by the release of water into the molten PET during processing. They are:

(a) localized hydrolytic degradation of the PET in the immediate vicinity of the hydroxide particles;

(b) local supercooling of PET down to T_{cc}, initiating crystallization right about the hydroxide particles.

The anticipated reduction of PET molecular weight, localized in the vicinity of the hydroxide particles, is expected to produce a low molecular weight tail in the molecular weight distribution of the polymer. This may be detected by determining the M_w/M_n ratio of samples containing Al(OH)$_3$ and pure PET of the same IV uniformly hydrolyzed during processing. Alternatively, comparison of GPC scans of the corresponding samples may yield the desired information. For this purpose specimens were extruded under identical conditions, all of which had an initial IV of 0.93 dL/g. For GPC purposes the aluminum hydroxide was carefully filtered off. Otherwise, the weight of Al(OH)$_3$ was taken into consideration in the calculations for other procedures.

The quality of the GPC curves was not high enough to allow a quantitative determination of the differences between the corresponding samples. Nevertheless, when superimposed the curves clearly indicated that the Al(OH)$_3$-hydrolyzed PET samples contained amounts of low-M polymer significantly larger than the comparable IV PET hydrolyzed in the absence of Al(OH)$_3$. Similar conclusions were obtained from analysis of M_w and M_n values of the same PET specimens. Typical results are presented in Table VI.

From the table it is obvious that the reduction in molecular weight by the most efficient Al(OH)$_3$ concentrations, of 0.75–1.00% is associated with a substantial broadening of the molecular weight distribution caused by the large drop in M_n. This is as expected from a substantial and nonuniform degradation of the PET.

The degradation of PET by 2–4% hydroxide permeates the whole volume of the polymer and does not stay localized close to the $Al(OH)_3$ particles. This is evident from the reduction of both M_w and M_n to essentially the same levels, independently of whether the hydrolysis was initiated by water released by $Al(OH)_3$ or uniformly present in the polymer. In this context we wish to recall that, at IV of ~0.3, the T_{cc} ceases to increase and, when normalized to IV of 0.50, and T_{cc} actually decreases.

In the melt water is presumed[3] to react quantitatively with PET:
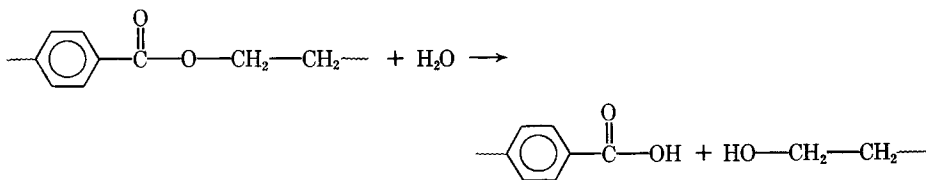
Calculations indicate that, for instance, $Al(OH)_3$ at 1% level can release at most 1.5 mol % water into the molten PET. In the case of PET IV = 0.93, having M_w = 87,700 and M_n = 58,800, the above amount of water is supposed to cause, on the average, 8.8 scissions per chain. This results in 9.8 fragments averaging M_w = 8900 with a corresponding IV of less than 0.20 dL/g. Our analysis indicate that for 1% $Al(OH)_3$ the degradation is far smaller. The WAXD scans of $Al(OH)_3$ retrieved from extruded PET showed that substantial fraction of the $Al(OH)_3$ did not lose water and change to $AlOOH$. The lower than anticipated PET degradation actually observed is, hence, understandable.

The second possible nucleation mechanism involves local supercooling of PET, brought about by the release of water into the molten polymer by the hydroxide particles. Calculations of heat (enthalpy) of formation of $AlOOH$ and water from $Al(OH)_3$, using ΔH_f values in *Lange's Handbook of Chemistry*[4] indicated the reaction to be endothermic. The calculations indicate that for each mole of water released in the liquid phase 1.95 kcal are absorbed from the environment, while 12.45 kcal are absorbed for each mole of water released in the gas phases. The difference in ΔH_f between the liquid and gas phases of the released water is almost completely due to the heat of vaporization of water. Under the assumption of complete decomposition of $Al(OH)_3$ to water and $AlOOH$, 1% $Al(OH)_3$ in the polymer releases 1.5 mol % water in the vapor state, resulting in an absorption of 187 cal from the surrounding molten PET. Now, the heat capacity of PET in the molten state right at T_m is C_p^l = 9.2 cal/mol·K.[5] The heat of fusion (crystallization) of PET, ΔH_c, is 534.6 cal/mol (2240 J/mol).[6] Our data show the average T_{cc} of well-nucleated PET to be around 215°C. Simple calculations indicate that 187 absorbed calories are sufficient to reduce the temperature of 15 mol % PET from 275°C to 215°C, and more than sufficient to reduce the temperature of 10 mol % polymer from 300°C to 215°C, and then induce the crystallization of either. The 1% by weight loading of $Al(OH)_3$ is, hence, capable of a sufficient reduction in temperature and the absorption of evolved heat of crystallization of a very substantial fraction of the surrounding PET. As we gather from Table II, 0.5% $Al(OH)_3$ is sufficient to effectively nucleate PET and increase the T_{cc} to levels close to that obtained from 1% $Al(OH)_3$. At this point we should recall that not all the $Al(OH)_3$ in most formulations is converted to AlOOH during processing (the converted fraction depends on processing con-

ditions). This indicates to us that a reduction in temperature and subsequent crystallization of significantly less than 5% of the PET are sufficient to nucleate the crystallization of all of the PET at about 215°C.

CONCLUSIONS

Metal hydroxides capable of releasing water within the processing temperature interval of PET are effective nucleating agents for the crystallization of the polymer. Hydroxides releasing water out of said interval do not nucleate PET. There are two proposed nucleation mechanisms: (a) a localized severe hydrolysis of PET by the water released in the immediate neighborhood of the hydroxide particles; (b) a localized supercooling of the PET in the vicinity of the particles by the released water. The hydrolyzed PET of sharply reduced molecular weight has a T_{cc} significantly higher than the T_{cc} of the unhydrolyzed majority of the polymer. Upon cooling from the melt, and with the possible localized supercooling, the PET in the immediate vicinity of the hydroxide particles crystallizes first, nucleating the rest of the polymer. At present, we cannot verify whether both mechanisms operate concomitantly and which one of them is dominant.

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