A DSC/TGA STUDY OF THE HETEROGENEOUS NUCLEATION OF CRYSTALLIZATION IN POLYPROPYLENE COPOLYMER

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SUMMARY

The study is aimed at the evaluation of the influence of nucleating agent (t-butyl)benzoic aluminum (NA) in changing clarity, crystallization temperature (T_p) and radiation resistant properties of polypropylene copolymer, PP (co) with 6% of ethylene. It has been shown that crystallization temperature of PP (co)+NA did not change when the content of the NA less than 2%, but the super cooling temperature is a little bit increased when the content of the NA was 2 or higher than 2%. Clarity of the blend comprising of PP (co)+NA decreases with the addition of 2% or more NA (t-butyl)benzoic aluminum. However, the increase of the supercooling temperature makes possible to improve radiation resistance of the material.

I - INTRODUCTION

Nucleating agents are added to polypropylene (PP) in order to obtain optimum physical properties. It has been reported that the addition of nucleating agent changes the polymer's crystallization temperature, spherulite size, density, clarity, impact and tensile properties considerably [1]. In this paper we report crystallization of a random copolymer of PP with 6% ethylene with a nucleating agent (NA), (t-butyl)benzoic aluminum, with its content varying from 0.1% to 2%. The random copolymer of PP with 6% ethylene has been particularly selected in view of its reported improved radiation stability compared to pure polyethylene due to lower crystallinity of the former [2]. Various crystallization parameters were estimated from Differential Scanning Calorimetry (DSC). Thermo-Gravimetric Analysis (TGA) has been carried out to assess thermal stability conferred upon propylene copolymer by the addition of nucleating agent.

II - EXPERIMENTAL

1. Materials

Polypropylene copolymer containing 6% ethylene was from Chisso Corporation, Japan. The NA used was (t-butyl)benzoic aluminum (Merck, Germany) and was used as such without further purification.

2. Mixing of materials

The mixing copolymer with nucleating agent was carried out using a "Haake" mixer (Germany) at 40 rpm and 140°C. The product was compressed into sheets by molding under a pressure of 150 kg/mm^2 for 3 minutes at 170°C using a space of 0.5 mm after preheating for 5 - 7 minutes at the same temperature. The hot sheets were then immediately cooled between the plates of a cold press at room temperature. For comparison of clarity, thin films were prepared by heat pressing the aforementioned sheet between aluminum foil at 170 - 180°C and under a pressure of 150 kg/mm^2.

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3. Measurements

For TGA/DSC studies, a Simultaneous Thermal Analyzer by Netzsch (Germany) was used. The measurements were carried out at a heating rate of 5°C min^{-1} for DSC studies. The cell was heated from room temperature to 185°C, and held for 15 minutes in order to eliminate any crystallization memory. Thermograms were acquired during the heating cycle and during the cooling cycle under static conditions. As all the experiments were carried out under identical setting, the data generated could be used to directly compare crystallization parameters. To ensure reproducibility of results, the measurements were done on at least 3 samples of each blend composition.

The thermal gravimetric analysis and DTA of the copolymer and the blends were carried out by taking the sample in the cell of the Netzsch (Simultaneous Thermal Analyzer) STA 509 with S:Pt thermocouple at a heating rate range 25 - 600°C and at a flow rate of 200 cm^3 min^{-1}.

III - RESULTS AND DISCUSSION

1. DSC Thermograms of crystallization of propylene copolymer and blends

As mentioned earlier, a factor of considerable importance is the influence exerted by varying amounts of the nucleating agent on the degree of supercooling of propylene copolymer denoted by a range of T_p-T_m. T_p is the peak temperature and occurs at the intercept of the tangents to the sides of the exothermic curve and it is a measure of the temperature when the bulk of the polymer has crystallized. *Fig.1* shows "closed loop" thermogram of the melting and crystallization of pure copolymer, the degree of supercooling exhibited is around 36.5°C (table 1).

Figure 1 shows two peaks belonging to pure copolymer and blend containing 2% NA. Prominent crystallization exotherm peaks were observed for the copolymer as well as blends with nucleating agent. A steady increase of about 6°C up to 2% of the nucleating agent was observed (table 1) resulting in the decrease in supercooling. In the mass production of medical supplies, it means that the molding cycle will be shorter and hence more economical.

Table 1: Values of various crystallization parameters of PP (co) in PP (co)+ NA blends from DSC and T_m values

T_m, °C	Sample	T_p, °C	T_{onset}, °C	T_c - T_p, °C	ΔW, mm	ΔH, J g^{-1}
156.5	PP (co)	120.0	129.0	7.5	10	95.01
156.4	PP(co)+0.1%NA	122.4	129.3	6.9	10	86.65
155.1	PP(co)+0.25%NA	122.8	128.0	5.2	10	63.71
154.7	PP(co)+0.5%NA	123.4	129.8	6.4	11	81.09
150.6	PP(co)+1.0%NA	124.3	130.0	5.9	9	78.03
150.0	PP(co)+2.0%NA	126.0	132.0	6.0	8	91.25

Various crystallization parameters estimated from the DSC thermograms included (*Table I*) T_{onset}, T_c-T_p, Si, ΔH and ΔW and the significance of these parameters are described here and illustrated for clarity in Fig. 2.

1. T_{onset} is the temperature of onset of crystallization which is the temperature when the thermogram initially vertically deviates from the baseline on the high temperature side of exothermal.

2. Another temperature described as the "constructed temperature" and referred to as T_c is obtained at the intercept of tangents to the baseline and high temperature side of the exothermic peak.

3. The rate of nucleation is also indicated by the parameter Si.

4. The quantity T_c-T_p indicates the overall rate

of crystallization. The smaller the value the greater the rate of crystallization.

5. The width at half-height of the exothermic peak is denoted by ΔW which is a measure of crystallite size distribution; the smaller the ΔW, the narrower the distribution and vice versa.

6. The quantity ΔH is the measure of the heat of crystallization. The unit of the ΔH is Joule but the specific heat of crystallization has a unit of Joule per gram ($J\ g^{-1}$) and it was calculated by dividing the ΔH (Fig. 2) by the weight of the sample taken for the DSC analysis [2].
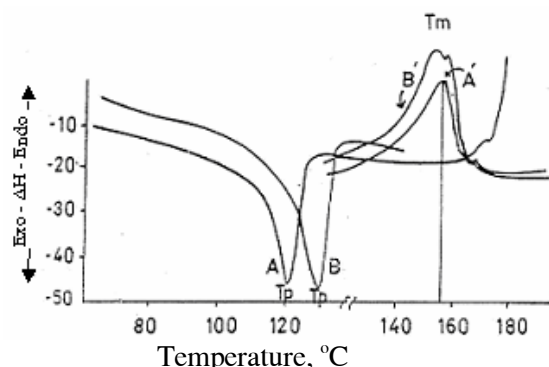

Figure 1: DSC exotherms of
(A) Crystallization curve of PP(co); (A') its melting curve; (B) Crystallization curve of PP (co) + 2.0% NA; (B') its melting curve

Table 2: Thermogravimetric analysis (TGA) of PP copolymer, PP (co), and PP (co) + NA, (t-butyl)benzoic aluminum, blends

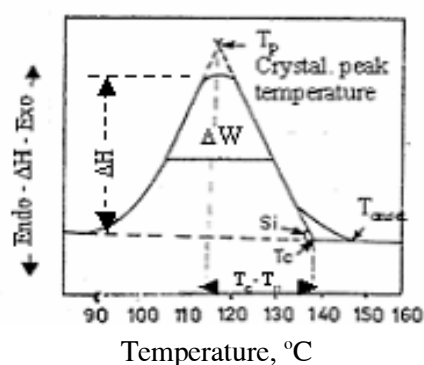| Nature of sample	Losses (%) at temperature (^{o}C)				
	10%	20%	40%	60%	80%
Pure PP (co)	290	320	350	-	400
PP(co)+0.1%NA	280	320	350	370	410
PP(co)+0.25%NA	280	320	350	370	410
PP(co)+0.5%NA	290	340	370	390	410
PP(co)+1.0%NA	320	350	400	415	430
PP(co)+2.0%NA	300	350	400	410	430

Figure 2: Schematic of the method of estimation of various crystallization parameters from the DSC crystallization exotherm peak (for the data shown in table 1)

T_c-T_p value was found to decline generally from pure copolymer to blends containing higher amounts of nucleating agent that demonstrates an increase in the overall rate of nucleation. With increase in T_p, the corresponding increase in T_{onset} would be expected which is indeed the case as exhibited by higher values of T_{onset}. Si value was found to increase progressively with the increase in quantity of the additive. An increase in Si upon addition of nucleating agent was observed in polypropylene by Beck et al. [1].

ΔW values were unchanged at lower content of the nucleating agent. However, a decline in value was observed in blends containing 1% or 2% as well as a narrow distribution. This presumably could be due to a faster rate of crystallization culminating in similar size of spherulites and thus narrower distribution.

The ΔH values were found to be low for the blends, demonstrating a low trend for 0.1, 0.25,

0.50 % of nucleating agent, but the sample containing 2% of NA registered an increase. Although a higher rate of crystallization is achieved, the NA appears to depress the heat of crystallization, presumably due to suppression of the activation energy barrier thus facilitating the formation of crystallites requiring less thermal input.

Prominent melting endothermic peaks of PP copolymer and its blends with NA were observed. T_m is found to decrease steadily, and a lowering of 6ºC in the blend containing 2% NA is observed (table 1). The decrease could be attributed to the depressing of melting point induced by impurities, as generally observed in the melting behaviour of organic compounds.

TGA of copolymer and blends

For the blend range containing 0.1% to 0.5% of NA, the thermograms show no improvement in thermal degradation rate, as shown in table 2. In the blend range 1% and 2%, considerable increase in temperature for losses of weight at 10%, 20%, 40%, 60% and 80% of the polymer was observed, indicating imparting of thermal stability to the blends by the nucleating agent.

Clarity of PP copolymer blends

The visual examination of thin films of copolymer, and those belonging to blends with NA, showed progressive increase in haze (lack of clarity) with the increase in amount of NA from 0.1 to 2 weight percentage. Our results agree with the observations of Zarah et al [3] who have concluded that the addition of the NA (t-butyl) benzoic aluminum did not improve the transparency, but a higher value of T_p was observed. This study, however, was confined to only addition of 0.1% NA and recording of only one of the crystallization parameters, T_p.

IV - CONCLUSION

Three desirable properties needed to be improved in polypropylene comprise clarity, an increase in crystallization temperature and radiation resistance. Somewhat moderate improvement in T_p (or degree of supercooling) has been observed on addition of NA. The clarity seems to be affected adversely on addition of higher amounts of NA. As regards radiation resistance, one may expect that with the decreasing amorphous fraction of PP in the copolymer, the radiation resistance will be also not favorably influenced due to morphology. The dependence of radical termination rates on percent crystallinity in gamma irradiated *iso-tactic* polypropylene has been reported by Dunn et al [4]. Gains in thermal stability associated with the addition of NA can be exploited in applications where clarity and radiation resistance may not be important considerations.

REFERENCES

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