Characterization of the Nucleation Efficiency Based on Crystallization Behaviour and Other Polypropylene Properties

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The more reliable values of the crystallization temperature were obtained from the non – isothermal DSC thermograms recorded at low cooling rate. The crystallization time was evaluated from the isothermal DSC thermogrames recorded at those temperatures at which the crystallization occurs. PP nucleated with Irgastab NA 21, has crystalline phase that contains the smallest spherulites, as compared to those nucleated with Irgastab NA 04 and Irgaclear DM. The incorporation of the nucleating / clarifying agents into the polymer matrix is homogeneous only if the melt processing conditions were well defined for each of them. A dependence on the molecular weight of the nucleated PP morphology was observed. The spherulite size decreases with the increase of the molecular weight.

Keywords: crystalization, nucleation, polypropylene, nucleating agent, spherulite.

Polypropylene (PP) is a semicrystalline polymer, that enclose relatively big spherulites in an amorphous matrix [1 – 3]. The PP morphology depends on the polymer chemical structure, the crystallization conditions and the impurities content. [3].

The "spontaneous" crystallization of polypropylene generally takes place, at low cooling rate and is due to the impurities and the structural defects around which the spherulites increase. The appearance and growth of the spherulites is known as nucleation. The spherulites appear following a «spontaneous» crystallization, have bigger sizes than the visible light wave length. Therefore, at the light passing through the PP morphology, is produced the light dispersion and thus the film blushing [1, 2, 4, 6, 9, 10].

If "artificial defects" / « impurities» like nucleating / clarifying agents, are dispersed into the polypropylene matrix, a « controlled crystallization » takes place. These agents increase, by many times, the crystallization rate. Because, in the same space, appears and grows a higher number of spherulites, their dimensions are smaller than the wave length of the visible light [1, 2, 7, 10].

So, if because of the "spontaneous" crystallization appear 10^6 crystallization centers / cm^3 which lead to the spherulite by $\approx$100 µm, in the " controlled" crystallization, 10^{12} crystallization centers / cm^3 appear which determine the formation of spherulites by approx. 1 µm. Because of the smaller spherulites size, the light will pass through the polymer, reason for which the film opacity ("haze") will decrease and its clarity will increase[1, 2].

The developed morphologies based on a "controlled crystallization" depend on the nucleating / clarifying agent, the polypropylene grade, the PP molecular weight and its polydispersity and also, by the melt incorporation conditions.

For high nucleation / clarifying efficiency, the agents must comply with the following conditions: non - soluble into the PP melt within the 115 – 140 ^{0}C temperature range (namely at the PP crystallization temperature). The control of the PP morphology cannot be performed if the agents are not wetted by the polymer or at least, absorbed by it, and if they are not evenly dispersed into the polymer matrix, in the finest dispersion possible (1 - 10µm) [1 – 10].

The obtaining of the desired morphology in a "controlled" way, allows the increase of the crystallization temperature, and the decrease of the crystallization time that means low melt processing time and increased output of the PP conversion processes [9]. The morphological changes determined by the nucleation improve the physical, mechanical and optical properties of the polymer, the dimensional stability, the cost - performance index and decrease the scrap formation at the melt processing.

The nucleated PP is suitable for a variety of applications: injection molding into thin wall packaging, furniture, house appliances, thermoforming of cups, trays, tubs, general blow molding. The control of PP optical properties makes possible its utilization as a substitute for the known transparent polymers [9, 10].

The PP "controlled crystallization" can be appreciated based on the comparative analysis of the polymer crystallization with and without nucleating / clarifying agent using the crystallization temperature and crystallization time. The crystallization temperature can be obtained from the non – isothermal DSC thermogrames and the crystallization time from the isothermal ones.

The paper aim is to find the appropriate conditions for the crystallization temperature and time measurement and to appreciate based on the finded conditions and another PP properties the nucleation efficiency of some nucleation / clarifying agents.

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Experimental part

Properties of PP having different molecular weights,(M_w) nucleated with different agents using the same additivation formula were analysed .

Materials

-PP with M_w of 320 000 (MFI = 1,.08g/10 min. - PP B 200 grade) and PP with M_w of 230 000 (MFI = 2.5 g/10 min.- PP F 401 grade).

-Nucleating / Clarifying agents (0,15 % w/w in all formulations): Irgastab NA 21 – phosphate derivate, Irgastab NA 04 – phosphate derivate, Irgaclear DM - sorbitol derivate.

-Additives for the PP melt processing.

Additives incorporation

After dosage, the additives were incorporated into polypropylene, in the solid state by mixing 10 min., in a mixer with a 3D rotation movement and in the melt by extruding, at 210 ^{0}C and 20 rpm. using a mono-screw extruder.

Characterization:

There were performed the following measurements:

- melting temperature (T_t) and crystallization temperature (T_{cr}) : DSC thermogrames recorded in two heating - cooling consecutive cycles – with 10 ^{0}C/min and 1 ^{0}C/min;

- crystallization time (t_{cr}) : DSC thermogrames recorded from 50 to 220 ^{0}C, with 10 ^{0}C/min, cooling at 120 ^{0}C and isothermal recording of the crystallization time at different temperatures. It was used a Du Pont 2000 thermo – analyzer ;

- the haze color index- STAS 8179/3-75 and ASTM 2457, on EVANS ELECTROSELENIUM England device;

-the gloss index-ASTM 203, on EVANS ELECTROSELENIUM England- device;

- the white index - ASTM 2134, on a Zeiss leucometer;

- the morphology: optical microscopy with polarized light, microscope POM - MC1-IOR type, equipped with a controlled heating-cooling device.

Results and discussions

The non - isothermal DSC thermograms of the PP with M_w = 320 000, with and without nucleation agents, recorded at 10 ^{0}C / min. heating / cooling rate are presented in fig 1. In these recording conditions, there is no difference between the four thermograms. It looks that in all cases, the PP melting takes place around 160 ^{0}C (fig.1a) and the crystallization in the 110 – 140 ^{0}C temperature range (fig.1b).

The same results were obtained in case of the non-isothermal thermogrames recorded with 10 ^{0}C / min. for the PP with M_w = 230 000 with or without nucleation agents (fig.2). In this situation too, it seems that, there is no difference between the thermograms of the PP with or without nucleation agent. It looks that in all cases the melt take place around 160 ^{0}C (fig.2a) and the crystallization within the 110 – 140 ^{0}C temperature range (fig.2b).

Big differences between the analyzed samples are illustrated by the thermograms recorded with 1 ^{0}C/min the cooling rate (fig.3, 4). It can be noticed that, in all cases the crystallization temperature has higher value for nucleated PP. The increasing of the crystallization temperature depends on the used nucleating agent and on the polymer molecular weight. For PP with high molecular weight (M_w = 320 000), the crystallization temperature increase,

depending on the used additive, with 3 – 7 ^{0}C. If PP has a smaller molecular weight than the crystallization temperature increase with 4 – 10 ^{0}C, as a function of the used nucleating agent. For the both PP, the smaller nucleation effect was registered for Irgastab NA 04 and the bigger effect in case of Irgastab NA 21 and Irgaclear DM.
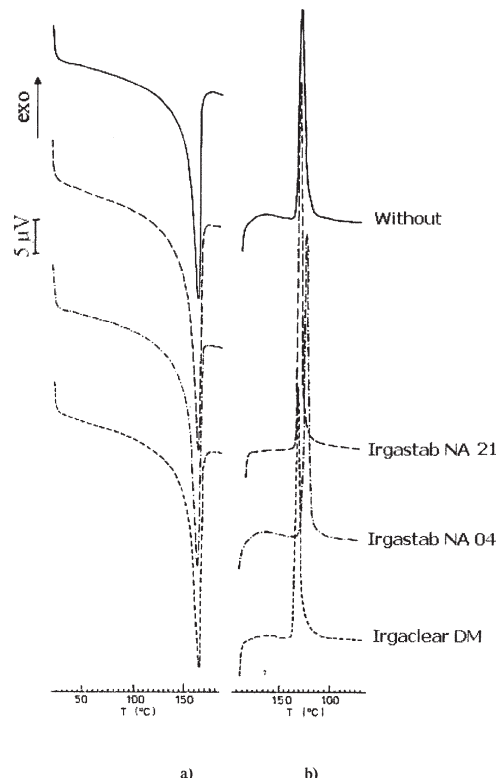

Fig.1 Melting and crystallization of the PP with M_w = 320 000 nucleated with Irgastab NA 21, Irgastan NA 04, Irgaclear MD. Non-isothermal thermograms recorded with the heating / cooling rate by 10 ^{0}C / min (a: the melting endothermes, b – the crystallization exothermes)
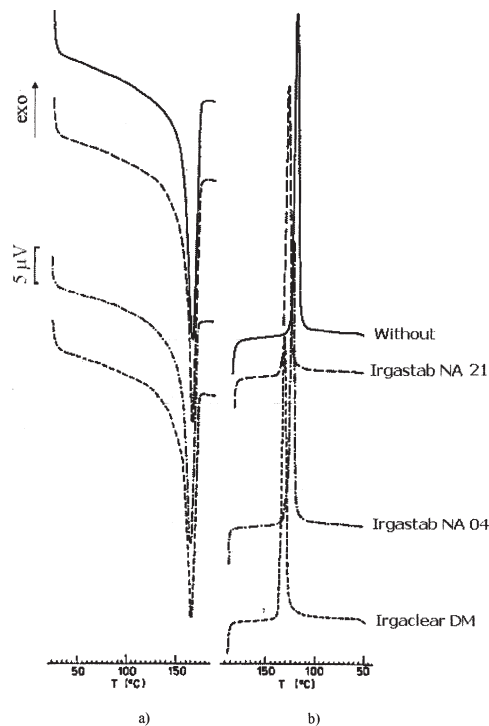

Fig.2. Melting and crystallization of the PP with M_w = 230 000 nucleated with Irgastab NA 21, Irgastan NA 04, Irgaclear MD. Non-isothermal thermograms recorded with the heating / cooling rate of 10 ^{0}C / min (a: melting endothermes, b – crystallization exothermes)

Based on these results it can be concluded that, for the PP crystallization temperature determination the DSC thermograms must be recorded in non isothermal conditions with small cooling rate, respectively at 1 ^{0}C/min.

The isothermal DSC thermograms

It was observed that, depending on its value, the temperature at which the crystallization time is measured, allows or not, the recording of the crystallization peak (fig.5). If, at 145 ^{0}C, the thermogram of the PP with M_w = 320 000 nucleated with Irgaclear DM do not contains any crystallization peak, at 143 ^{0}C this peak is just shaped. At 140^{0}C, the recording allows the measurement of a crystallization time of 17 min (fig. 5a). Depending on the nucleating agent, at 140 ^{0}C, the crystallization peak of nucleated PP has different shape (height, width and area - fig. 5b). Knowing that the crystallization time control the injection molding cycle it is clear that a shorter crystallization time increase the output of the conversion processes. Irgastab NA 21 and Irgaclear DM are good PP nucleating agent because they shorten the crystallization time with about 15 – 17 min.
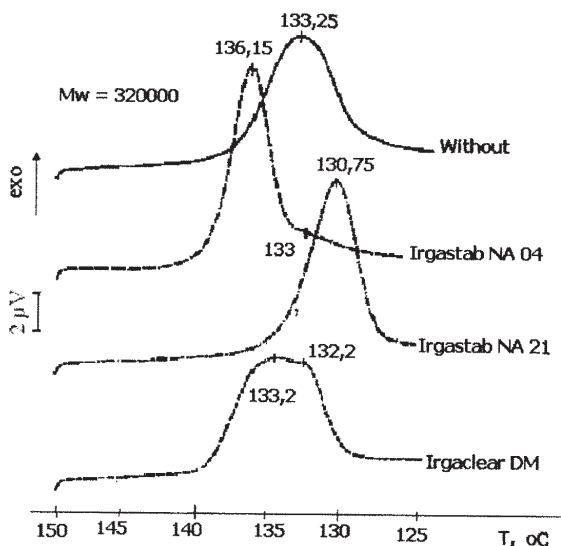

Fig.4 The non - isothermal crystallization with the cooling rate of 1 ^{0}C / min of the PP M_w = 230 000 with or without nucleation agents

Fig.3. Non - isothermal crystallization with 1 ^{0}C / min cooling rate of the PP M_w = 320 000 with or without nucleation agent

Fig.5. PP isothermal crystallization (a - PP with M_w = 320 000 nucleated with Irgaclear DM; b- PP with M_w = 320 000, without nucleating agent or nucleated with Irgastab NA 21 or Irgaclear DM

Considering the data presented in table 1 it can be observed that the used nucleating agents decreases the crystallization time for PP with M_w = 320000 with 9 – 16 min. and with 4 – 15 min. for the PP with M_w = 230000 .

The nucleated PP that has the highest crystallization temperature and smallest crystallization time has also the smaller haze, highest gloss and highest white degree. This observation does not depend on the polymer molecular
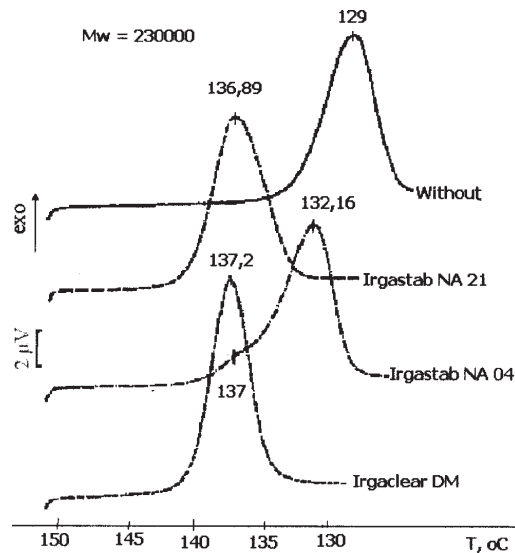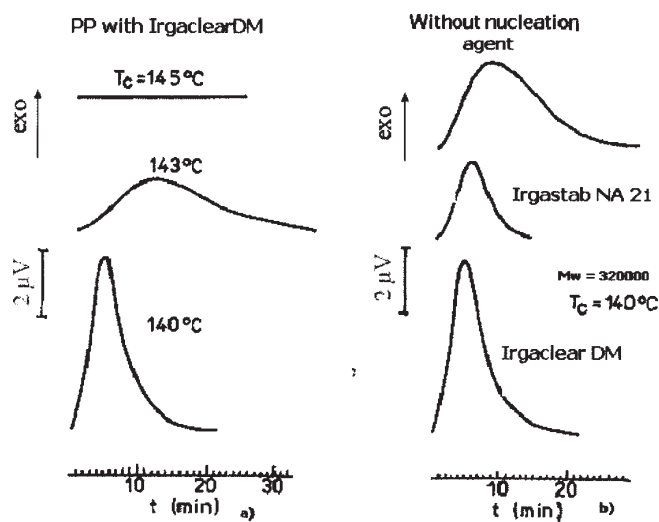
weight. It can be also observed that the nucleation does not change the starting melting temperature or the maximum of melting temperature.

The figures 6 and 7 prove that in case of the nucleating agent presence, the spherulites are much smaller, especially in the case of PP with bigger molecular weight (fig.6). Even all the nucleating agents were incorporated into the PP matrix in the same conditions the resulted

Table 1

PROPERTIES OF PP WITH DIFFERENT MOLECULAR WEIGHT NUCLEATED WITH DIFFERENT AGENTS

Properties	PP, M_w = 320 000				PP, M_w = 230 000			
	N9	N10	N11	N12	N 13	N 14	N15	N16
T crystallization, °C	111.4	**118.8**	111.3	114.88	116.1	**126.12**	120.68	120.49
Time crystallization , [min.]	29.34	**13.88**	20	21.28	25.2	**10.1**	17	18.5
T onset, °C	150,4	150,1	150,2	150,0	150,5	150,15	150,2	150,3
Tpeak , ^{0}C	151,5	151,6	151,6	151,4	151,5	151,6	151,6	151,6
ΔH, μVs/mg	100,05	**83**	99,66	97,125	89,55	88,174	81,260	92,869
Gloss, %	35	**41**	31	40	44	**49**	36	42
Haze, %	39	**23.3**	38.2	23.3	32	**26**	40.6	25.6
White degree, %	23.81	**29.89**	29.29	29.69	28.20	**30.05**	28.92	28.30

Fig. 6a. PP M_w = 320 000 , without nucleating agent

Fig.6b. PP M_w = 320 000 with Irgastab NA 21
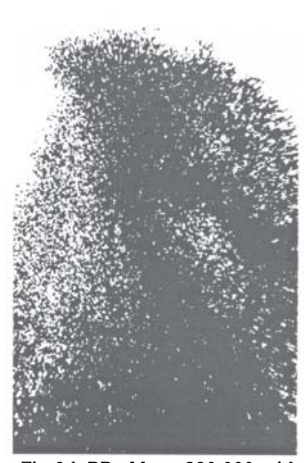
Fig. 6c. PP M_w = 320 000 with Irgastab NA 04

Fig.6d. PP M_w = 320 000 with Irgaclear DM

Fig.7a. PP MFI = 2.5 g/10 min., without nucleating agent

Fig.7b. PP MFI = 2.5 g/10 min., with Irgastab NA 21

Fig.7c. PP MFI = 2.5 g/10 min., with Irgastab NA 04

Fig.7d. PP MFI = 2.5 g/10 min., with Irgaclear DM

morphology are inhomogeneous, especially in case of Irgastab NA 04 .

Considering the morphologies presented in figures 6, 7 and bearing in mind the above presented results it can be noticed that the nucleated PP with the smallest crystallization time has the most regular and order crystalline phase and the smallest spherulites (fig.6 b and 7 b) The nucleating agent responsible for such a behaviour is Irgastab NA 21. In case of Irgastab NA 04 the obtained morphologies are strongly irregular, and contains small spherutiles near bigger ones, even tthan those from un-nucleated PP. For the same nucleation agent like Irgastab NA 21 the morphology of PP with M_w = 320000 contains smaller spherulites than those formed in case of the PP with M_w = 230000 nucleated with the same agent.

All the studied nucleating agents were incorporated in the same conditions. It is possible that responsible for the observed morphological heterogeneity to be the incorporation conditions. Depending on the chemical structure, it is possible that every nucleation agent to need suitable incorporation conditions.

All the above illustrate a dependence on the molecular weight of the nucleated PP morphology. Otherwise in [11,12] it was demonstrated that shear induce crystallization of PP is also influenced by the molecular weight values. Because in case of PP with greater

molecular weight the new spherulites are smaller the haze improving is almost 50% higher than that in case of the PP nucleated with the same agent but with smaller molecular weight.

Conclusions

The more reliable values of the crystallization temperature were obtained from the non – isothermal DSC thermograms recorded at low cooling rate. The crystallization time was evaluated from the isothermal DSC thermograms recorded at those temperatures at which the crystallization occurs.

The nucleated PP that has the highest crystallization temperature and smallest crystallization time has the most regular and order crystalline phase with smallest spherulites and also the smaller haze, highest gloss and white degree.The nucleating agent responsible for such a regular and order crystalline phase with smallest spherulites is Irgastab NA 21.

It was demonstrated a dependency on the molecular weight of the morphology of nucleated PP. Because the morphology of the nucleated PP with M_w of 320 000 contains smaller spherulites, the haze improving is almost 50 % higher than that in case of the nucleated PP with M_w of 230 000 of which morphology contains bigger spherulites.

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