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EFFECT OF RECYCLING PROCESS IN TWIN SCREWS EXTRUDER HAAK ON STRUCTURE AND CRYSTALLIZATION BEHAVIOUR OF POLYPROPYLENE

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ABSTRACT

Recycling process of polypropylene (PP) in twin screws extruder HAAK at high (195 - 230°C) and low (175-190°C) temperature ranges was studied. IR spectra and solubility of recycled samples show that neither oxidative degradation nor network formation has occurred at recycling conditions. So only degradation of PP molecules to smaller fractions may take place, that contributes to increasing of Melt Flow Index (MFI) of recycled samples. The results show also the stronger effect of recycling temperatures on the structure changes than that of number of recycling times. We can see also the structure changes of recycled PP cause the higher crystallization rate, higher crystalline percentage of spherulite formations with smaller dimensions. It leads to higher crystallization temperatures (3-4°C) but lower melting temperatures (4-5°C) of recycled PP in comparison with virgin PP.

Key words: *Recycled PP, crystallization, structure changes.*

I - INTRODUCTION

Polypropylene (PP) is one of the most widely used thermoplastic resins due to its numbers of advantages. However, the big mass of used PP causes serious environmental problems because they hardly deteriorate in natural conditions. So one of the best ways to solve these problems is recycle used PP, which has also significant economic effect.

Recycling process for PP is often carried out in extruders (single- or twin screws). In these conditions polymer suffer thermal and mechanical destructions that lead to numbers of structural changes [1]. These changes have inevitable effects on crystallinity of recycled PP and, as consequences, on other mechanical properties. Therefore, it is important to study the effect of recycling process on structure changes and crystallization behavior of PP. It helps to evaluate the properties changes and so the possibility of further application of recycled PP.

Consequently, the aim of this work is evaluating the effect of recycling process in twin screws extruder on structures and crystallization behavior of PP.

II — EXPERIMENTAL

1. Materials

PP resin used in this work is the homopolymer PPH7060 supplied by Total Petrochemical Company (USA) with MFI 12 g/10 min. (230°C; 2.16 kg); specific gravity 0.905 g/cm^3.

2. Measurement methods

MFI is determined according to ISO 1113 on equipment KAYENESS Inc. (USA) at temperature 230ºC and compression loading 2.16 kg;

Morphology of PP samples is studied on polarized optical microscope LEICA DC 300 (Germany).

IR spectra are taken from PP films thickness about 25 μm on EQUINOX 55 FTIR Spectrometer, BRUCKER Company.

3. Recycling procedure

The process is carried out in twin screws extruder HAAK with the length to diameter ratio (L/D) of 40:1 at two temperature ranges: low range (175-190ºC), denoted as PPT, and high range (195-230ºC), denoted as PPC. The screw speed is kept constant (300 rpm) and number of recycling times is up to 7.

III - RESULTS AND DISCUSSION

1. Structure changes in the recycling process

In figure 1, the polarized optical microscopy pictures of recycled PP are presented. As shown on the pictures, the spherulites structure of PP is existed in all studied samples but with different size. Obviously, the more numbers of cycles, the smaller spherulite size of recycled PP. This phenomenon is observed for PP recycled both at low (175 - 190ºC) and high (195 - 230ºC) temperature ranges. Also, we can see spherulite size decreases dramatically when the temperature increases, while these changes occur not so fast with increasing number of cycles. That means the recycling temperature has stronger effect on spherulite size than number of cycles.

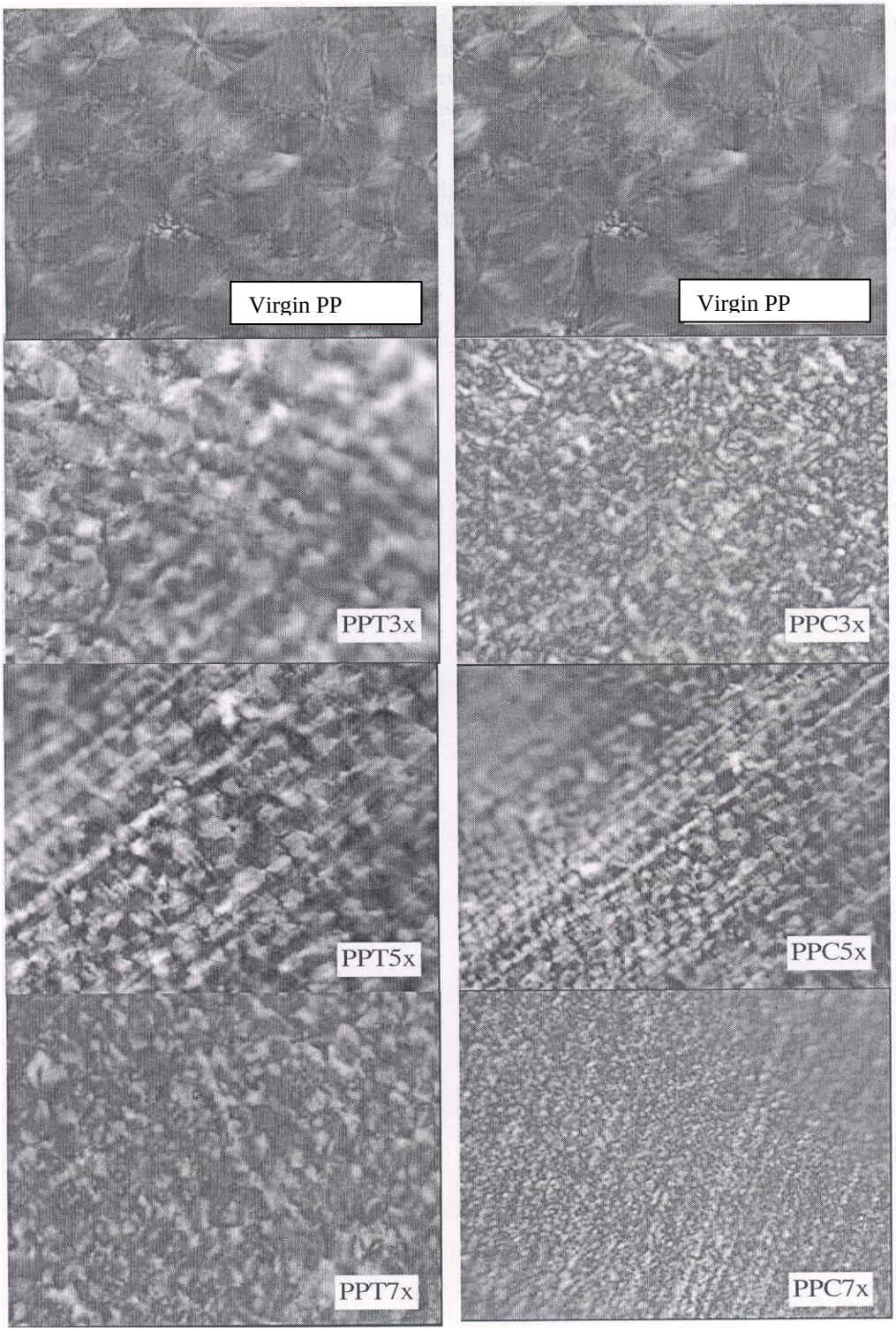
Decrease of spherulite size should have effect on melt flow index (MFI) of polymer. Indeed, MFI measurements show higher values with higher number of recycling times (table 1).

Table 1: Effect of number of recycling times on MFI of recycled PP (twin screws extruder HAAK, 300 rpm)

Samples	Number of recycle time	Recycle temperature, ºC	MFI, g/10 min (2.16 kg, 230ºC)
Virgin PP	0		10.7
PPT 1	1	175-190	10.4
PPT 2	2		10.8
PPT 3	3		11.8
PPT 5	5		12.9
PPT 7	7		13.5
PPC 1	1	195-230	13.2
PPC 3	3		14.4
PPC 5	5		16.2
PPC 7	7		20.3

Again, we can see from table 1 that MFI of recycled PP raise faster with temperature: after 7 recycling times at 175 - 190ºC the MFI increases only for 2.8 g/10 min. in comparison with virgin PP. However, when recycling temperature range is 195 - 230ºC, only after one cycle MFI gets the value of 2.5 g/10 min higher than that of virgin PP. This indicates to more considerable effect of temperature on recycling process.

MFI measurement shows also some decrease after 1st cycle at low temperature (10.4 g/10 min. vs 10.7 g/10 min. of virgin PP). It may be due to network formation in recycling process, but this network quickly destroyed in following recycling times. The complete

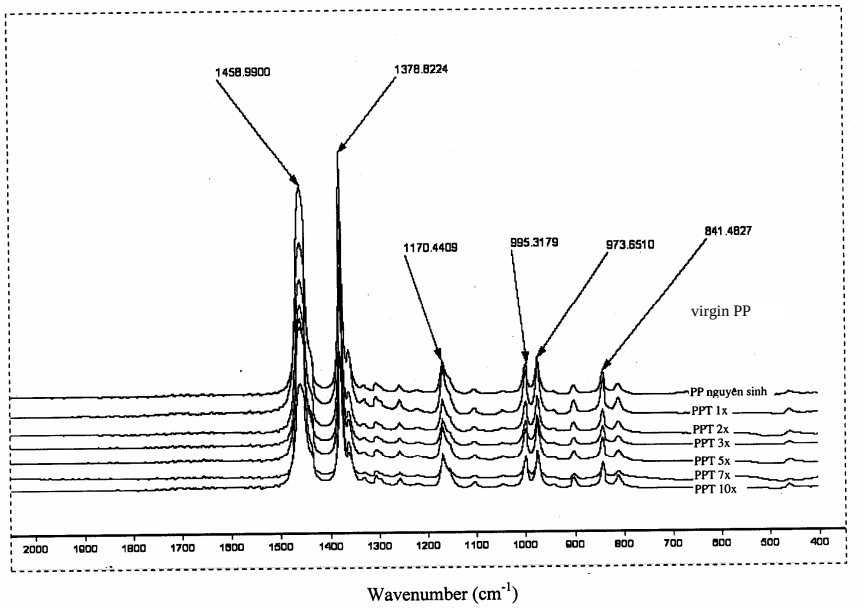


(a) (b)

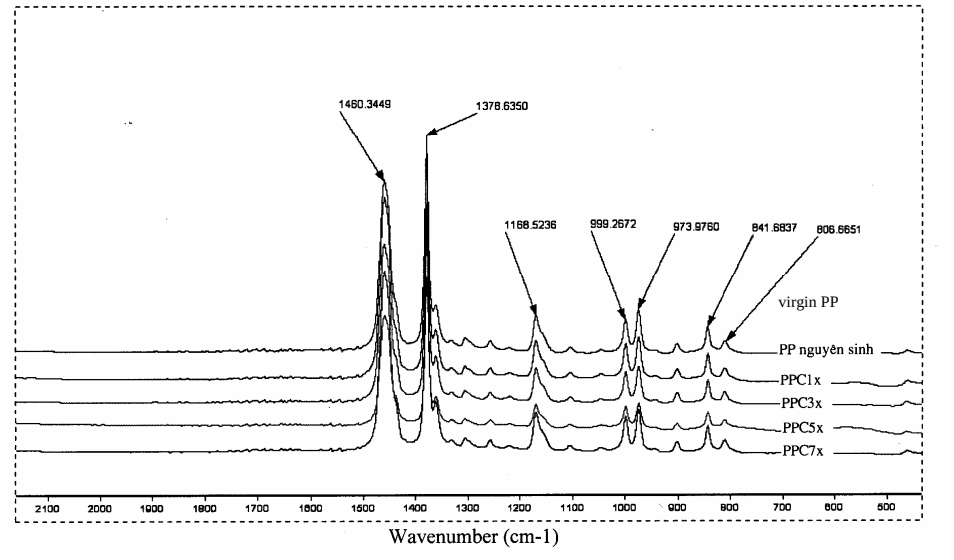
Fig. 1: Effect of number of recycled times on morphology of PP, observed in polarized optical microscope at low (a) and high (b) temperature

solution of all tested samples in toluene indicates to absence of network formations in recycled PP. So, increasing of MFI values may be contributed by 2 factors: mechano-thermal degradation in extrusion process that leads to lower molecular mass and lower spherulite size of recycled PP.

To examine the changes in chemical structure of recycled PP molecules, the IR spectra of virgin and recycled PP were analyzed (figure 2).



a- Recycling temperatures 175 - 190°C



b- Recycling temperatures 195 - 230°C

Fig. 2: IR-spectra of virgin and recycled PP for various numbers of recycling times

From Fig. 2 obviously that for both recycling temperatures ranges no visible changes in chemical structure of recycled PP occurred. We can see good coincidence of

characteristic peaks of virgin and recycled PP The absence of peak corresponding to carbonyl group in the region 1500-1800 cm^{-1} shows that oxidative degradation does not occur in this case. This may be explained by general absence of oxygen inside extruder and relative modest recycling temperature. These results fit well with other authors [2], when they studied on thermal and mechanical degradation of PP.

Analysis of above experimental results allows propose that recycling process in twin screws extruder leads only to molecular degradation to lower mass fractions. Neither oxygen combination to PP molecules, nor network formation has occurred in recycling process.

2. Nonisothermal crystallization of recycled PP

Nonisothermal crystallization of recycled PP was studied through DSC examination. As we reported before [3], the following parameters were collected from DSC diagram of recycled PP (temperatures 195-230ºC): T_0, T_t - onset and terminal crystallization temperatures; T_p - peak of crystallization temperature; T_m - melting temperature. These parameters were summarized in table 2.

Table 2: Thermal properties of recycled PP at high temperature profile (195-230ºC)

	T_0, ºC	T_p, ºC	T_t, ºC	T_m, ºC	X, %	t, min	Z, min^{-4}
PP	125.3	111.2	101.3	167.6	42.4	2.40	166.7
PPC1	126.7	113.5	103.2	165.6	43.3	2.35	186.0
PPC3	127.7	114.9	104.8	164.8	43.9	2.29	210.2
PPC5	127.8	115.4	106.7	163.7	44.8	2.11	299.8
PPC 7	127.5	115.7	107.1	162.5	45.4	2.04	349.5

- PPC means recycled PP at high temperatures. The number denoted the recycling times.

Obviously, recycled PP has higher temperature at peak of crystallization T_p and for PPC5-PPC7 this temperature difference consists of 3 - 4ºC in comparison with virgin PP. Also, temperatures of beginning and terminal crystallization are higher for recycled PP. On contrary, melting temperatures of recycled PP are remarkably lower than that of virgin PP.

From DSC data, the other parameters are calculated:

- Crystallization time t:

$$t = (T_0 - T_t)/\lambda$$

where λ - cooling rate, equals 10 K/min. for this study.

- Crystallinity percentage X:

$$X\% = (\Delta H/\Delta H_{100}) \times 100\%$$

Where ΔH - enthalpy of analyzed sample (J/g); ΔH_{100} - enthalpy corresponding to the standard thermal crystallization value of 100% crystalline polymer sample. For PP the ΔH_{100} is 209 J/g [4].

- Speed constant of crystallization Z:

Parameter Z is calculated from Avrami equation:

$$1 - X = \exp(-Z.t^n)$$

In this equation, the Avrami number is defined as the sum of two factors: crystalline growth geometry (a) and nucleation (b). If crystallines growth in one dimension (rod like formations), a = 1; in two dimensions (disk like formations) a = 2; in three dimensions (spherulites etc.) a = 3. Number b = 0 if nuclei are formed immediately at beginning and kept constant in whole process. If the nuclei are formed occasionally during all crystallization process, b = 1. So in our study, the POM pictures above show spherulite structures in recycled PP, that means 3-dimensional development of crystalline formations (a = 3).

Beside, we can suggest that crystalline nuclei may be formed occasionally during all crystallization process (b = 1). These suggestions allow accept the Avrami number n = 4, so the Avrami equation for recycled PP in this study has the following form:

$$1 - X = \exp(-Z.t^4)$$

From respective calculated values of X and t (see table 2) the speed constant Z is calculated for every recycling time of PP (see table 2).

Data presented in table 2 show the higher crystallinity percentage (X), shorter crystallization time (t) and higher crystallization rate (Z) of recycled PP in comparison with virgin PP. This difference becomes more clearly when the number of recycling times is increases. The reason of this phenomenon may be as follow.

In recycling process, the PP molecules degrade to smaller fractions. It leads to some consequences: a- the higher quantity of possible nuclei of crystallization; b- higher mobility and shorter relaxation time of molecules fractions. Due to these consequences, the crystallization occurs with higher rate and at higher temperature. However, high crystallization rate and high quantity of nuclei will create more crystalline with smaller dimensions. It quite fit with DSC date (smaller melting temperature) and POM pictures of recycled PP (Fig. 1).

IV - CONCLUSIONS

Recycling process of PP in twin extruder may lead to degradation of molecules to smaller fractions. Neither oxidative degradation nor network formation has occurred in this process. At the recycling, the temperature range has stronger effect on structure change than that of number of recycling times.

Structure changes in recycling process will promote the formation of smaller crystallines of recycled PP than that of virgin PP. It is due to high mobility and short relaxation time of small molecular fractions in recycled PP. It leads to higher crystallization rate as well as crystallinity percentage of recycled PP in comparison with virgin PP.

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