Thermal Analysis of Some Physico - mechanical Properties of Polypropylene (PP) Used for Manufacturing of Performance Sport Items

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This paper presents the influence of processing temperature on the physico-mechanical properties of polypropylene (PP) used at the injection molding of performance sport items. The test-pieces were molded at the following real injection temperatures: 220, 240, 260, 280 and 300°C. It was determined that the in-mould pressure decreases with the increase of processing temperature The thermal analysis performed were: TG, DSC and DMA. It was established that the processing temperature influences the thermal stability of the polymer molded at 300°C, but the vitrification temperature and the melting temperature are slightly influenced by the processing temperature. The storage modulus E' is influenced by the processing temperature and stress frequency.

Keywords: polypropylene (PP), injection molding, Thermogravimetry (TG), Differential Scanning Calorimetry (DSC), Dynamic-Mechanical Analysis (DMA)

Polypropylene is a thermoplastic material with 60-70% cristallinity degree, opaque in large thickness products and translucide in small ones. As other polyolefins, the PP colour is milky-white and the touch feeling is similar to wax. PP density is 900-1020 kg/m^3, but it can exceed 1020 kg/m^3 when PP is reinforced with fiber glass, mica or talc. As at the other macromolecular compounds, the PP mechanical properties depend on molar mass. These are orientation-sensitive, meaning that the PP mechanical properties are higher if the macromolecules are oriented in the stress direction. This orientation of the melted macromolecules can lead to an increase of the crystallization degree and can be considered at PP injection, respectively, at feeding the melt flow into the mold cavity, by the proper choosing of the injection points. PP has a good impact resistance at the room temperature [1], but this resistance is lower as the temperature is decreasing. The polypropylene-ethylene copolymer has a much better impact resistance than the PP homopolymer, due to the $–CH_2 – CH_2$- sequences of the copolymer which provide a high damping capacity [2].

The reinforcement materials are widely used for improvement of PP mechanical properties [3]. Filling PP with magnesium silicate, the tensile breaking strength, rigidity and impact strength are higher [4]. Filling PP with fiberglass (30%), doubles the tensile breaking strength and increases the elastic modulus and fatigue strength [5]. Filling the PP homopolymer with 40% talc, the elastic modulus increases from approx. 1500 MPa to 4300 MPa.

PP is a thermoplastic polymer which has the following advantages: excellent price/quality ratio [6], it can be coloured in a wide tints palette, it is a low density material, its dimensional stability is not influenced by humidity, it is easy to process. All these features recommend PP for utilization in various high performance fields.

The main application fields of PP are:

- automotive industry (e.g., bumpers, side protection strips, housings, guides, cockpit module, etc.,) [13];
- packaging industry (e.g., packages for foodstuff, for storage and transport of liquids, etc.);
- garden furniture industry (e.g., chairs, lounge chairs, tables, benches, etc.);
- household items (cups, bowls, buckets, etc.) , textile industry, cosmetics industry.

Besides these application fields, PP is used at manufacturing of sport items for:

- skating (e.g., rigidizing inserts of boots for speed roller skates, outer shell of ice skates boots, different types of buckles and clips for street roller skates, etc.),
- cycling (e.g., pedals, components for speedometer, buzzer, headlamp, etc.),
- snowboarding (e.g., inner rigidizing inserts of boots, protective plate of gloves, etc.);
- sport footwear (e.g., the sole for athletic shoes).

At the injection molding of polymeric materials, the characteristics of molded products are highly influenced by the processing temperature, pressure of the flowing-state material during filling the mold cavity and the mold temperature [7-9,12].

This paper analyzes the variation of some PP physico-mechanical properties depending on the processing conditions. The results were obtained through thermal analysis methods applied to polypropylene homopolymer, grade INNOVENE 100- GB06 used for manufacturing of performance sport items.

Experimental part

The test-pieces were molded from PP homopolymer, grade INNOVENE 100- GB06 using an ENGEL injection molding machine, type G/11/10/116/3. The temperature of the flowing-state material was measured with a thermocouple DYNISCO, type Ti422J fit in the nozzle of the plasticizing cylinder in order to get the real temperature within the central stream of the polymer melt flow.

The following real injection temperature were set: 220, 240, 260, 280 and 300°C. The in-mold cavity pressure was determined using a IDA transducer made by Dynisco Europe GmbH. For all processings, the parameters were set as follows: injection pressure at 1600 bar, injection speed at 20 mm/s and the temperatures of plasticizing cylinder and cilynder nozzle were set according to the required parameters. The molded test-pieces were examined through thermal analysis. For some comparative determinations were also used raw polymer granules in

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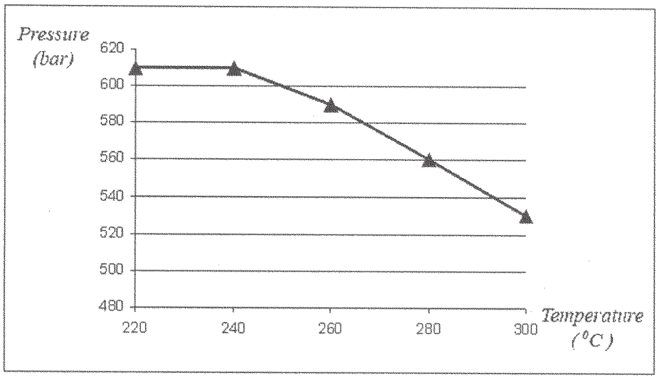

Fig.1. The dependence of in-mould pressure peak on the real injection temperature for PP homopolymer, grade INNOVENE 100- GB06

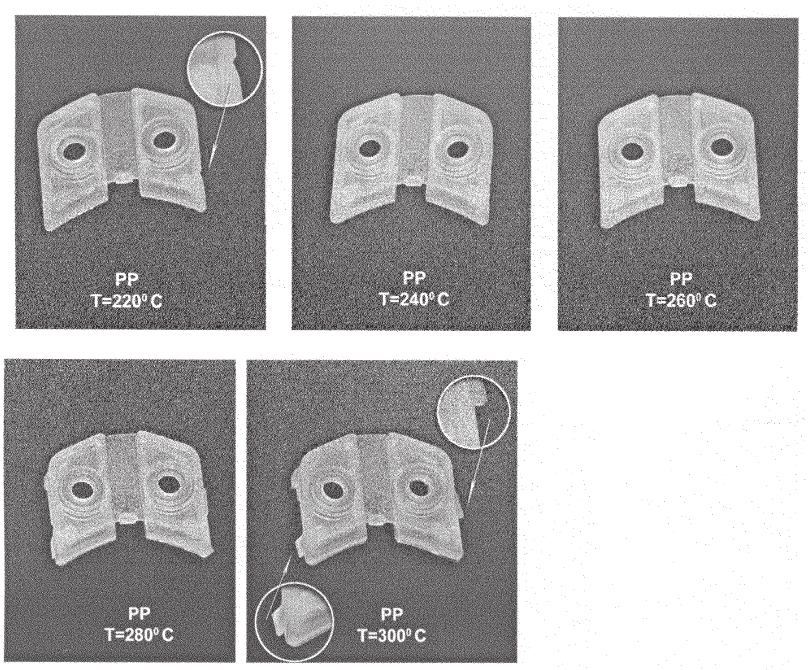

Fig.2. The influence of injection temperature on the quality of test-pieces molded in PP homopolymer, grade INNOVENE 100- GB06

order to see the changes occurring in material during injection.

The thermogravimetry (TG) analysis was carried out using a NETZSCH analyzer, typeTG 209 as follows: under nitrogen atmosphere, temperature interval 20-990°C, heating rate of 5 °C/min.

The Differential Scanning Calorimetry (DSC) determinations were accomplished using a DSC calorimeter NETZSCH, type 204 as follows: in nitrogen atmosphere, heating from 20 to 220°C with a rate of 10 °C/min, cooling at - 100°C with a rate of 10 °C/min, isothermal regime at -100°C for 5 min., heating from -100 to 400°C with a rate of 5 °C/min.

The Dynamic-Mechanical Analysis (DMA) was made using a NETZSCH analyzer, type DMA 242 C as follows: in air atmosphere, temperature interval -30 and + 150°C, heating rate 1°C/min, at a strain frecquency of 0,5; 1; 2; 5 and 10 Hz applied in dual cantilever bending mode.

Results and discussions

If the injection parameters were maintained constant during all five processing temperatures, it was determined that the real in-mold pressure decreases from 610 bar when processing at 220°C to only 530 bar when processing at 300°C (fig. 1) This fact is explained by the slow decrease in viscosity of the polymer melt.

The test-pieces molded at five processing temperatures are presented in figure 2. The test-piece molded at 220°C

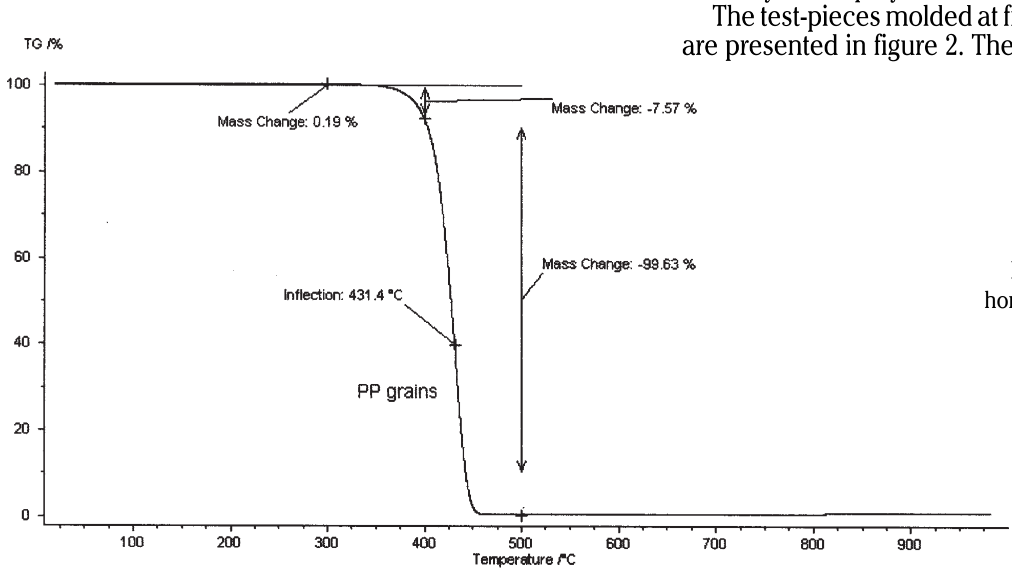

Fig. 3. TG diagram for PP homopolymer granules, grade INNOVENE 100- GB06

Processing temperature of PP [°C]	Inflection [°C]	Mass loses [%] up to the temperature [°C] of		
		300	400	500
granules	431.4	0.19	7.57	99.63
220	431.2	0.17	7.81	99.59
240	431.3	0.18	7.62	99.62
260	431.1	0.17	7.88	99.60
280	431.0	0.16	7.70	99.61
300	420.9	0.38	16.29	99.63

Table 1
MASS LOSSES FOR PP HOMOPOLYMER, GRADE INNOVENE 100- GB06 PROCESSED AT DIFFERENT TEMPERATURES

is qualitatively non-compliant as the mold cavities were not filled completely. The test-pieces molded at 240 and 260°C are qualitatively compliant as the mold cavities were filled completely, their surfaces are free of melt flow marks or burrs and no degradation of polymer occured as well. The test-piece molded at 280°C is qualitatively non-compliant as burrs are present. The test-piece molded at 300°C is qualitatively non-compliant as its surface has visible marks of polymer thermal degradation. Out of these remarks, it results that, in the specified injection conditions, the optimum processing temperature ranges between 240 and 260°C. The defect of the test-piece molded at 220°C, (incomplete piece with surface bearing visibile marks of melt flow, which are usually due to the polymer mechanical degradation into the plasticizing cylinder), can be eliminated by a slight increase in screw rotation speed, meaning that an increase in the shearing speed determines the decrease in viscosity of the polymer melt and the complete filling of mold cavities.

TG diagram for PP homopolymer granules, grade INNOVENE 100- GB06 is shown in figura 3.

The curves for the analyzed six test-pieces are not represented all in one single figure because the values are very close and the curves overlapping is almost perfect. The inflection points on TG diagrams and the mass losses up to 300, 400 and 500°C are presented in table 1.

The inflection points on the TG diagram represent the temperatures where the decomposition rate is maximum. From table 1. it can be noted that the processing temperature has a very slight influence on the values of the inflection points. Due to thermal degradation occurred at the test-piece molded at 300°C, its value of the inflection point is different than the values of other pieces. For granules and processings at other temperatures (220, 240, 260 and 280°C), the inflection points have close values. The same is noted regarding the mass losses up to 300 and 400°C, respectively. Taking into account the previous remarks, the conclusion is that the best results are obtained by processing within the termperature interval 220 - 280°C. Defects of the test-pieces molded at 220 and 280°C can be eliminated by changing the screw rotation speed. At 280°C a slight decrease in screw rotation speed leads to an increase in viscosity of the polymer melt and, respectively, at non-formation of burrs on the molded test-piece.Values of melting temperatures T_t (the endotherm peak on the DSC curve) for PP homopolymer, grade INNOVENE 100- GB06, processed at different temperatures, are presented in table 2.

It can be noted that T_t varies between 162.2°C and 163.6°C, therefore the modifications are insignificant. Hence the processing temperature influences very little the melting temperature of PP homopolymer, grade INNOVENE 100- GB06.

Table 2
MELTING TEMPERATURES FOR PP HOMOPOLYMER, GRADE INNOVENE 100- GB06 PROCESSED AT DIFFERENT TEMPERATURES

Processing temperature of PP [°C]	T_t [°C]
granules	162.9
220	162.2
240	162.2
260	163.5
280	163.1
300	163.6

During the DMA determinations on all test-pieces, it was established that stress frequency has a major influence both on the storage modulus (E') and loss tangenta (tan δ).

Values for storage modulus (E') at - 30°C, relative to different stress frequencies and processing temperatures, are shown in table 3. From table 3 it may be noted that the stress frequency influences the values of storage modulus (meaning that E‘ increases as the stress frequency increases) and that the results are concordant with the theory related to temperature-time analogy [10,11]. According to this theory elaborated by M.L. Williams, R.F. Landel and J.D. Ferry, at increasing of applying frequency of force, the fluctuation network has no time to react and the material behaves as if the determination temperature would be lower (the initial stress frequency is mentioned).

From table 3 it can be noted that E' is largely influenced by the processing temperature. Increasing of the processing temperature determines the decreasing of the storage modulus (E') value.

The results for the peak of the loss tangenta (tan δ), values which can be assimilated with the vitrification temperature, are shown in table 4.

The processing temperature has a slight influence on the vitrification temperature values, while increasing the stress frequency leads to increasing of the vitrification temperature.

Stress frequency [Hz]	Value of E` [MPa] at the specific processing temperature [°C]				
	220	240	260	280	300
10	940	919	900	881	840
5	928	900	882	850	830
2	920	890	868	844	822
1	910	880	860	835	808
0,5	902	870	852	826	800

Table 3
VALUES OF E' AT -30°C RELATIVE TO STRESS FREQUENCY AND PROCESSING TEMPERATURE

Stress frequency [Hz]	Tan δ peak values [°C] at the specific processing temperature [°C]				
	220	240	260	280	300
10	13.5	13.8	14.3	14.5	15.0
5	13.1	13.2	14.1	14.2	14.4
2	12.0	12.2	12.6	13.2	13.6
1	10.2	10.6	11.0	11.4	11.7
0,5	8.3	8.8	9.2	9.8	10.1

Table 4
VALUES OF TAN δ RELATIVE TO STRESS FREQUENCY AND PROCESSING TEMPERATURE

Conclusions

We have studied the modification of physico-mechanical properties for PP homopolymer, grade INNOVENE 100- GB06, used at injection molding of high performance sport items. The injection molding machine employed was an ENGEL model G/11/10/116/3 and the test-pieces were molded at different processing temperatures, as follows: 220, 240, 260, 280 and 300°C. It was determined that by increasing the processing temperature, the real in-mold pressure decreases. Decomposition phenomenon occurs at 300°C processing temperature, by appearance of yellow-brown coloured burns on surface of the molded test-pieces.

TG analysis performed with a NETZSCH analizer, model TG 209, proved that the test-piece of PP homopolymer, grade INNOVENE 100- GB06 processed at 300°C has the lowest thermal stability due to thermal degradation. The thermal stability modifications of the test-pieces processed at other temperatures are rather insignificant compared with the thermal stability of raw material (granules). Hence the thermal stability is not affected within the processing interval of 220 - 280°C.

The determinations of T_t through DSC were accomplished using a DSC calorimeter NETZSCH, type 204. It was established that the melting temperatures are slightly influenced by the processing temperature and that no modifications occur compared with the raw material (granules).

The DMA determinations were performed with a NETZSCH analyzer, type DMA 242 C. These revealed that stress frequency has a major influence both on the storage modulus (E') and loss tangenta (tan δ). The values of E' and tan δ increase at increasing the stress frequency, confirming the specialty literature data. Increasing of the processing temperature determines decreasing of the storage modulus (E') value, but the values of vitrification temperature (tan δ) are slightly influenced. Based on these experimental results, the recommended processing temperature interval is 220 and 280°C.

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