

Study by Thermal Methods of Some Physical-Mechanical Properties of Polypropylene (PP) Used for High Performance Sport Products

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Abstract: This paper presents the influence of processing temperature on some mechanical-physical properties of polypropylene (PP) used for injection moulding of performance sport products. The test pieces were moulded at the following real injection temperatures : 220°C, 240°C, 260°C, 280°C and 300°C. It was determined that the in-mould (cavity) pressure decreased with increasing of the processing temperature. Also PP was thermally analyzed through : Thermogravimetry (TG), Differential Scanning Calorimetry (DSC) and Dynamic-Mechanical Analysis (DMA). It was established that processing temperature has a minor influence on the thermal stability, the glass transition temperature and melting point of polymer, but the storage modulus (E') is significantly influenced by the processing temperature.

Key words: polypropilene, injection moulding, Thermogravimetry (TG), Differential Scanning Calorimetry (DSC), Dynamic-Mechanical Analysis (DMA).

1. Introduction

The most used polymers for injection moulding of performance sport products are the following: polyoxymethylenes (POM, polyacetal), polyamides (PA), thermoplastic polyurethanes (TPU), polycarbonates (PC) and polypropylenes (PP) [1].

The polypropylene is used for manufacturing of sport products which do not require high levels of mechanical strength, rigidity and impact strength. The polypropylene has the following advantages [2]:

- excellent price/quality ratio,
- large range of colours,
- light material (density 900-1020 kg/m³),
- very good dimensional stability (moisture sensitive-free),
- easy processability.

The polypropylene was used during the 70's - 80's decades at manufacturing of ski boots, but it has to be replaced with thermoplastic polyurethanes (TPU) and polyamides (PA), as a result of its poor impact strength at low temperature. The Izod impact strength at - 30°C is very low (1,4 KJ/m²). For this reason, polypropylene was reinforced with different materials in order to improve its mechanical properties. Using magnesium silicate as a filler of polypropylene leads to the increase of breaking strength and impact strength [3]. The reinforcement of polypropylene with fiber glass double its ultimate tensile strength (tensile strength at break) and the elongation elastic modulus is increasing [4].

The polypropylene is used for manufacturing of sport shoe inners [5], inserts for football shoes, bicycle pedals, height adjusting device of motorscooters, etc.

The characteristics of the injection moulded polypropylene products are influenced by the temperature of polymer and by the pressure of the flowing-state material at filling the mould cavity.

This paper is an analysis of the variation of some mechanical-physical properties of polypropylene depending on the processing conditions. The results were obtained through thermal analysis methods applied to the polypropylene, grade Homopolymer Resin 100 GB06 used for manufacturing of performance sport items

2. Experimental part

The test-samples were moulded in polypropylene, grade Homopolymer Resin 100 GB06 using an ENGEL injection moulding 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 plasticizing cylinder nozzle in order to get the real temperature within the central stream of the polymer melt flow.

The following real injection temperature were set: 220°C, 240°C, 260°C, 280°C and 300°C.

The in-mould (cavity) pressure was determined using a IDA transducer made by Dynisco Europe GmbH. For all the processings, the parameters were set as follows:

- injection pressure = 1600 bar,
 - injection speed = 20 mm/s
- and the temperature of plasticizing cylinder and of cylinder nozzle were set according to the required parameters.

The moulded test samples were examined through thermal analysis. However, for some comparative determinations, there were used also raw polymer grains in order to see the material alterations during injection.

The thermogravimetry (TG) analysis was carried out using a NETZSCH analyzer, type TG 209 as follows:

- under helium atmosphere,
- temperature range 20-990°C,
- heating rate of 5 K/min.

The Differential Scanning Calorimetry (DSC) determinations were accomplished using a DSC calorimeter NETZSCH, type 204 as follows:

- under helium atmosphere,
- heating from 20 °C to 220°C, with a rate of 10 K/min,
- cooling at -100°C with a rate of 10 K/min,
- isothermal regime at -100°C for 5 min,
- heating at 400°C with a rate of 5 K/min.

The Dynamic-Mechanical Analysis (DMA) was made in dual cantilever bending mode on a NETZSCH analyzer, type DMA 242 C as follows:

- under air atmosphere,
- temperature range - 30°C and + 150°C,
- heating rate of 1 K/min,
- stress frequency of 0,5; 1; 2; 5; and 10 Hz.

3. Results and discussion

If the injection parameters were maintained constant for all the five stages of processing temperatures it was determined that the real in-mould pressure decreases from 610 bar for processing at 220°C to only 530 bar for processing at 300°C (Fig. 1).

This fact is explained by the major decrease in viscosity of the polymer melt. At increasing of injection temperature, the in-mould (cavity) pressure peak, (i.e., the maximum pressure needed to compact the material into the cavity) is decreasing till 530 bar at 300°C temperature.

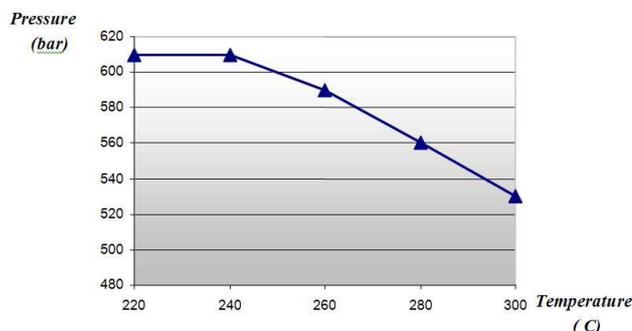


Figure 1. The dependence of in-mould pressure peak on the real injection temperature for PP, grade Homopolymer Resin 100-GBO6

Figure 2 shows qualitative aspects of the test pieces moulded between 220 - 300°C.

The quality of the piece moulded at 220°C is inadequate since the mould cavity was not completely filled with material and consequently, the piece is not completely contoured. The pieces moulded at 240°C and 260°C have an adequate quality since the mould cavity was completely filled, the surface of piece is free of melt flow marks, burrs or shrinkage and no degradation of polymer occurred. Raising the real injection temperature above this level leads to a deterioration of quality.



Fig. 2. The influence of real injection temperature on the quality of PP moulded parts (grade Homopolymer Resin 100 GBO6).

Thus, the piece moulded at 280°C has burrs and the surface of the piece moulded at 300°C is qualitatively inadequate as burrs are combined with visible marks of polymer's thermal degradation.

Concluding, for PP, grade Homopolymer Resin 100 GBO6, the optimal injection processing temperature is ranging between 240°C and 260°C and the optimal pressure peak for this temperature range is 590 – 610 bar. Specimen samples from these moulded pieces were cut in order to be thermally analyzed.

In Figure 3 is represented the TG diagram for PP grains and in Table 1 are presented the inflection points on TG diagram, and the mass losses at 300°C, 400°C and 500°C.

The inflection points on TG diagram represent the temperatures where the decomposition rate has a maximum. Table 1 shows that the values of inflection points and mass losses are slightly influenced by the processing temperature.

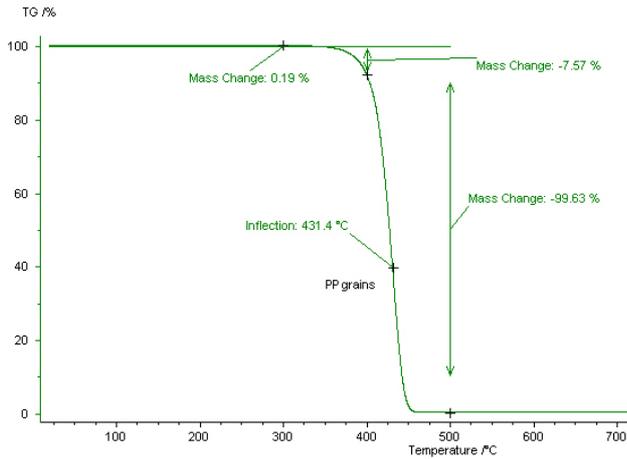


Figure 3. The TG diagram for PP grains

Concluding, the thermal stability of PP (grade Homopolymer Resin 100 GBO6) is not influenced by the processing temperature.

In Table 2 are presented the values for glass transition temperature T_v (the maximum of $tg \delta$ on DMA diagram) and melt temperature (the endotherm peak on the DSC curve) depending on the processing temperatures.

It can be noticed that T_v rises a little with increasing of the processing temperature, while the is insignificantly influenced by the processing temperature.

The DMA determinations for all test pieces establish that stress frequency have a major influence on the storage modulus (E'). In Tab. 3 are presented the values of storage modulus (E') measured at -30°C relative to different stress frequencies and processing temperatures.

It can be remarked from Tab. 3 that stress frequency influences the values of storage modulus (E') - E' increases as the stress frequency increases - meaning that the results are concordant with the theory related to time-temperature analogy [6,7]. 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 the determination temperature would be lower (with mentioning of the initial stress frequency).

TABLE 1. Mass losses for PP processed at different temperatures

Processing temperature of PP [$^\circ\text{C}$]	Inflection [$^\circ\text{C}$]	Mass loss [%] at specific temperature [$^\circ\text{C}$]		
		300	400	500
granule	431,4	0,19	7,57	99,63
220	431,2	0,17	7,81	99,59
240	431,4	0,18	7,87	99,60
260	431,5	0,18	7,95	99,61
280	431,6	0,19	8,10	99,62
300	431,9	0,20	8,29	99,63

TABLE 2. Glass transition temperature and melt temperature for PP processed at different temperatures

Processing temperature of PP [$^\circ\text{C}$]	T_v [$^\circ\text{C}$]	T_i [$^\circ\text{C}$]
Granule	14,0	162,9
220	13,5	162,2
240	14,0	162,2
260	14,4	163,5
280	14,7	163,1
300	15,0	163,6

TABLE 3. Values of storage modulus E' at -30°C temperature relative to stress frequency and processing temperature

Stress frequency [Hz]	E' [MPa] values for specific processing temperature [$^\circ\text{C}$]				
	220	240	260	280	300
10	940	920	890	860	840
5	930	910	880	850	830
2	920	900	870	840	820
1	910	890	860	830	810
0,5	900	880	850	820	800

From Table 3 it can be noticed that E' is largely influenced by the processing temperature. Increasing of processing temperature determines decreasing of material rigidity and lowering of storage modulus (E') value.

4. Conclusions

We have studied the modification of physical-mechanical properties for polypropylene (PP), grade Homopolymer Resin 100 GBO6 used at injection moulding of sport products.

The injection moulding machine employed was an ENGEL, model G/11/10/116/3 and test pieces were moulded at different processing temperatures, as follows: 220°C, 240°C, 260°C, 280°C and 300°C.

It was determined that the real in-mould (cavity) pressure decreases as a result of the viscosity decrease in melting polymer. Also it was determined that the test pieces are not completely moulded (incompletely contoured) at 220°C, while burrs are present and thermal degradation marks are visible on the surface of the test pieces moulded at 280°C and 300°C.

The TG analysis performed with a TG 209 NETZSCH analyzer proved that the thermal stability of PP (grade Homopolymer Resin 100 GBO6) is not influenced by the processing temperature.

Determinations of melt temperature T_t through DSC method were accomplished using a DSC calorimeter NETZSCH, type 204 and it was established that T_t is slightly influenced by the processing temperature.

Also the increase of processing temperature leads to a slight increase of glass transition temperature.

The DMA determinations for all test pieces were performed with a NETZSCH analyzer, type 242 C and it revealed that stress frequency have a major influence on the storage modulus (E'). Moreover, the values for storage modulus (E') rise as the stress frequency rise, confirming the specialty literature data. Increasing of processing temperature determines decreasing of storage modulus (E') value.

Based on these experimental results, 240°C and 260°C is recommended as the optimal processing temperature range.

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