Thermal Analysis of Some Mechanical-Physical Properties of Polyoxymethylenes (POM) used for Manufacturing of Performance Sport Products

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This paper presents the influence of the processing temperatures on the physical–mechanical properties of polyoxymethylenes (POM) used in injection molding of high performance sport products. The test-pieces were obtained by processing POM at the following temperatures: 180°C, 190°C, 200°C, 210°C, 220°C, 230°C and 240°C. It was established that the pressure in the mold decreases as the processing temperature increases. Further, thermal analyses (TG, DSC and DMA) were performed and it was noticed that the processing temperature had an influence on the thermal stability of the polymer, but the vitrification temperatures (T_v) and the melt temperatures (T_t) were poorly influenced by the processing temperature.

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

Polyoxymethylenes, sometimes called polyacetals, are high crystalin macromolecular compounds having a regular structure of methylenic ethers [1]. POMs own a combination of mechanical properties which build their reputation of high-performance thermoplastic materials destined to replace metals:

- remarkable resistance at alternate stress (fatigue),
- high strength at repetitive impact occured at low temperatures (- 40°C),
- high frictional and wear resistance,
- optimum balance between rigidity and elasticity,
- low creep sensitivity,

POMs are rigid materials with an exceptional dimensional stability used within a wide range of temperature (between - 50 and + 90°C). Besides these remarkable properties, POMs can be processed easily and coloured in a wide tints palette. Due to their high degree of crystallinity, POMs have better general mechanical properties (especially, rigidity) than other thermoplastics within the range of temperature 50 - 120°C. All these features recommend POMs for utilization in various high performance fields.

The main application fields of POM as material for technical products are in the automotive industry (e.g., toothed wheels and gears, housings, guides, active parts of oil or diesel pumps, gasoline-level floats, valves, etc.) and in the machine-building industry (e.g., gears, toothed racks, valves, chain links, screws, disks, cams, articulated rods, etc.[2].

The reinforcement of POMs with 25% glass fiber doubles their breaking strength, triples their tensile strength and considerably increases their rigidity. The frictional and wear resistance of POMs can be improved by reinforcement with molibden disulphur or teflon.

Besides the two application fields already mentioned, POMs are used for manufacturing of sport articles for skating, alpine skiing and snowboard, cycling, golf and tenis, alpinism, water sports and for footwear as well. For instance, as cycling applications, the toothed wheels for bicycle gear shifters, the components of the chain anti-skid system, the brake hand lever mechanism, all these are made of POM.

In alpine skiing and snowboard, the buckles and closing clamps of ski and snowboard boots are made of POM, as well the bindings components. In footwear, the flat sole and the spikes for golf shoes, the studs for football boots, the bootlace rings of alpinism and mountaineering boots - these are made of POM too.

In many specialty works [3,4], it is analyzed the variation of the physical-mechanical properties depending on the used temperature.

At polymers injection molding, the characteristics of the molded products are highly influenced by the processing temperature and pressure of the flowing state material at filling the mold cavity [5,6]. To fill the mold cavity, the injection process of POM requires a higher injection pressure and a longer time of hold pressure than other polymers (e.g., polyamide 6.6 or HDPE) due to the POM's very low melt flow rate [7]. The variation of pressure and temperature of the flowing state polymer occured inside the mold cavity has three distinct stages starting with the intrusion of melt: filling – compacting - solidifying and cooling of melt [6, 8].

In this paper it is analyzed the variation of some mechanical-physical properties, depending on the processing conditions of the polyoxymethylene (POM), grade Tenac 2013A used for manufacturing of performance sport items.

Experimental part

The test-samples were molded in polyoxymethylene (POM), grade Tenac 2013A 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 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: 180, 190, 200, 210, 220, 230 and 240°C. The in-mold cavity pressure was determined using an IDA transducer made by Dynisco Europe GmbH. For all the processings, the parameters were set as follows: injection pressure at 1900 bar, injection speed at 20 mm/s and the temperatures of plasticizing cylinder and cylinder nozzle were set according to the

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required parameters. The molded test-pieces were examined through thermal analysis For some comparative determinations, there were used also raw polymer grains in order to see the material modifications during injection.

The thermogravimetry (TG) analysis was carried out using a NETZSCH analyzer, typeTG 209 as follows: in nitrogen 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: in nitrogen atmosphere, heating from 0 °C to 180°C, with a rate of 10 K/min, cooling at 0°C with a rate of 10 K/min, isothermal regime at 0°C for 5 min., heating at 400°C with a rate of 5 K/min. The Dynamic-Mechanical Analysis (DMA) was made using a NETZSCH analyzer, type DMA 242 C as follows: in air atmosphere, temperature range - 50 and + 150°C , heating rate 1 K/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 the all seven processing temperatures, it was determined that the real in-mold pressure decreases from 1900 bar when processing at 180°C to only 1700 bar when processing at 240°C (fig. 1). This fact is explained by the slow decrease in viscosity of the polymer melt.

In figure 2 are shown the pieces molded at the seven different processing temperatures. The pieces moulded at 180°C and 190°C are not qualitively compliant as the mold cavity was incompletely filled (at 180°C) and because the piece surface bears melt flow marks, the result of a too low molding temperature, a non-homogenized polymer in injection cylinder, respectively (at 190°C). The pieces molded at 200, 210, 220 and 230°C are qualitively compliant as the mould cavity was completely filled and the surface is free of melt flow marks or shrinkage and no degradation of polymer occured. The piece molded at 240°C is qualitatively non-compliant as its surface has visible marks of thermal degradation of polymer. As a conclusion of these observations, the optimum processing temperature is ranging between 200 and 230°C.

In figure 3 are represented the TG diagrams for POM grains and POM molded at 180°C; in table 1. are presented the inflexion points on TG diagrams and the mass losses up to 200°C, 300°C and 400°C.

The inflexion points on the TG diagram represent the temperatures where the decomposition rate is maximum. From table 1 it can be noticed that the values of the lowest inflexion points are corresponding to the polymer processed at 180°C, 190 and 240°C, respectively. This fact can be explained by the too low viscosity of melt at the 180 and 190°C processings causing mechanical degradation of polymer and by thermal degradation of polymer which occurs during the 240°C processing. For grains and for the processings at other temperatures, the values of inflexion points are similarly close. The same thing is noticed regarding the mass losses up to 200 and 300°C, respectively. Taking into account the previous observations in conjunction with the figure 2, the conclusion is that the best results will be secured by processing at 200, 210, 220 and 230°C.

In table 2 there are values of the vitrification temperature T_v (i.e., the inflexion point of the DSC curve) and of the processing temperature T_t (i.e., the endotherm peak on the DSC curve), both relative to the processing temperature.

It may be noted that T_v varies between 144.6 and 147.4°C, while T_t varies between 174.5 and 177.3°C, therefore the modifications are insignificant. Concluding, the processing temperature has a minor influence on the transition temperatures for POM, grade Tenac 2013A

Through the DMA determination it was established for all test pieces that the stress frequency have a major

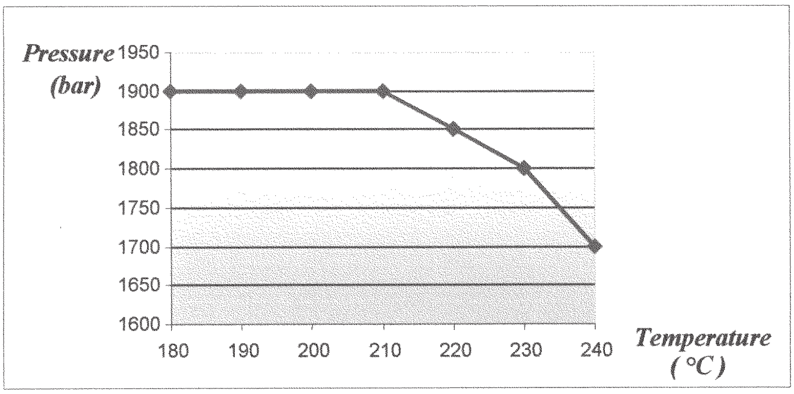

Fig.1. The dependence of in-mould pressure peak on the real injection temperature for POM, grade Tenac 2013A

Table 1
MASS LOSSES FOR POM PROCESSED AT DIFFERENT TEMPERATURES

Processing temperature of POM [°C]	Inflexion [°C]	Mass loses [%] up to the temperature [°C]		
		200	300	400
grains	354.9	0.13	12.04	99.56
180	318.0	2.56	34.60	99.52
190	327.2	2.40	30.76	99.95
200	351.8	0.32	13.44	98.75
210	351.4	0.46	13.05	99.13
220	350.6	0.53	12.58	98.10
230	352.3	0.22	12.90	99.30
240	344.7	1.84	27.51	99.66

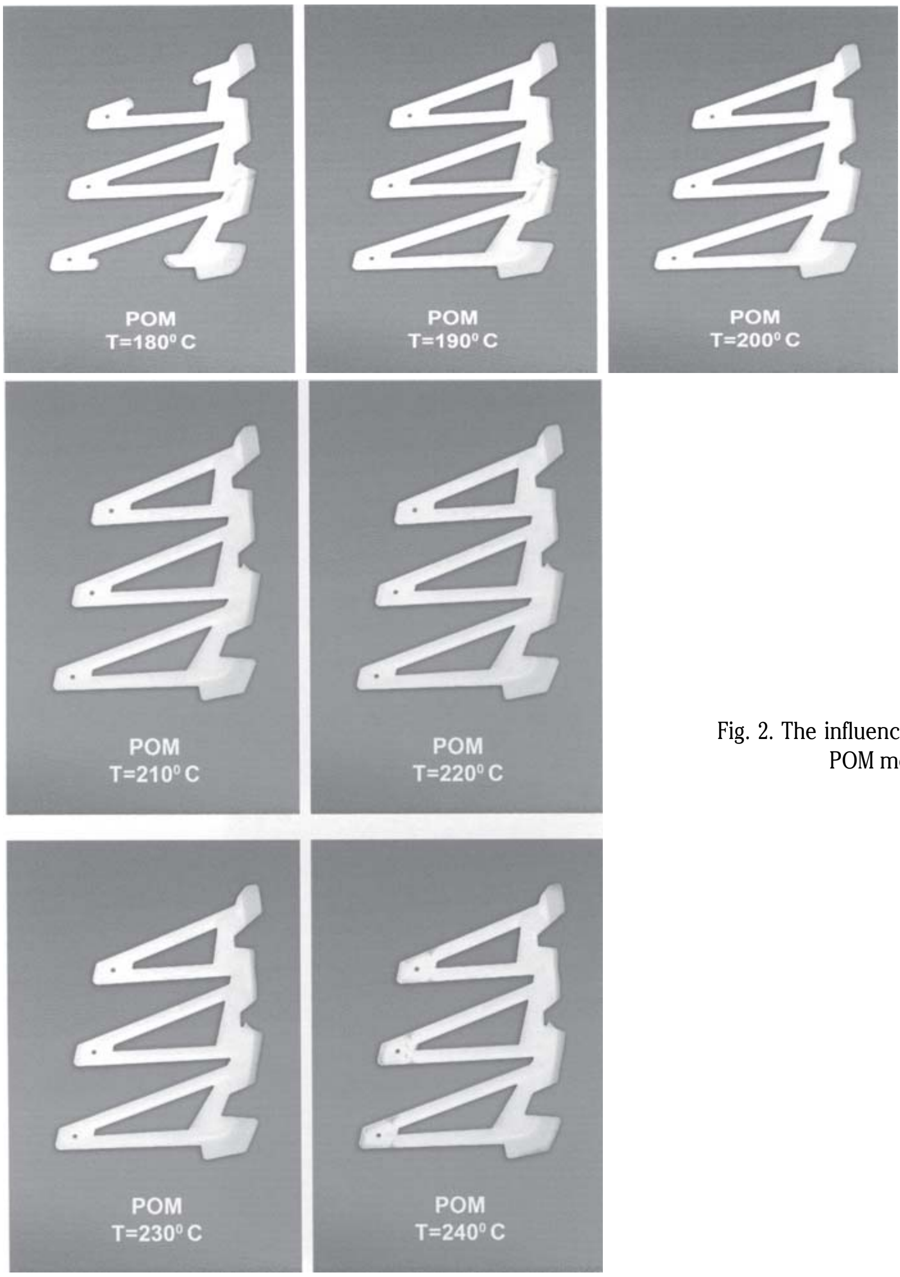

Fig. 2. The influence of injection temperature on the quality of POM molded parts (grade Tenac 2013A)

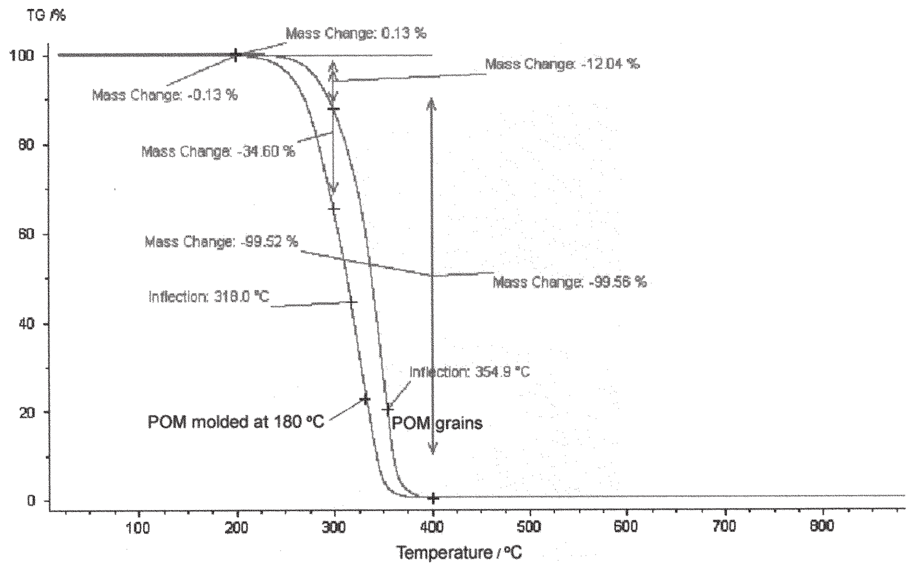

Fig. 3. TG diagrams for the test-pieces as POM grains and POM molded at 180°C

influence on the storage modulus (E') and on the loss tangenta (tan δ). In table 3 are shown the values for the storage modulus (E') at - 50°C temperature relative to different stress frequencies and processing temperatures.

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 time-temperature analogy [9,10]. According to this theory

Processing temperature of POM [°C]	T_v [°C]	T_t [°C]
Grains	144.6	174.5
180	145.5	176.1
190	145.2	176.9
200	147.4	176.9
210	147.0	176.4
220	144.9	176.6
230	147.4	177.3
240	145.7	175.2

Table 2
VITRIFICATION TEMPERATURE AND MELT TEMPERATURE FOR POM PROCESSED AT DIFFERENT TEMPERATURES

Table 3
VALUES OF E' AT - 50°C TEMPERATURE, RELATIVE TO STRESS FREQUENCY AND PROCESSING TEMPERATURE

Stress frequency [Hz]	Value of E` [MPa] at the specific processing temperature [°C]						
	180	190	200	210	220	230	240
10	890	895	810	815	820	823	900
5	885	880	805	810	810	817	890
2	880	865	800	800	805	810	880
1	870	860	798	790	795	800	875
0.5	865	855	795	780	784	790	867

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

Stress frequency [Hz]	Values of peak tan δ,[°C] at the specific processing temperature [°C]						
	180	190	200	210	220	230	240
10	140.1	141.2	144.5	144.0	143.6	144.4	141.8
5	138.7	139.2	141.1	142.0	140.8	141.6	139.0
2	135.0	135.2	140.0	140.1	138.9	138.2	136.8
1	134.2	134.0	137.7	138.8	137.1	136.6	132.0
0.5	133.2	133.8	135.1	136.7	134.4	134.1	130.2

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 (with mentioning of the initial stress frequency).

From table 3 it may be noted that E' is largely influenced by the processing temperature. The values determined at 180, 190 and 240°C are different than the ones at other processing temperatures. However, these values are concordant with the determinations obtained through TG analysis, confirming that the material is mechanically degraded, and thermaly degraded, respectively, at these temperatures.

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

The values for vitrification temperature are slightly influenced by the processing temperature (however, the same conclusion was obtained through the DSC analysis), but the increase of stress frequency leads to increase of the vitrification temperature. The difference between the vitrification temperatures obtained through DSC and DMA analysis are due to the different determination modalities and different heating rates as well.

Conclusions

We have studied the modification of physico-mechanical properties for polyoxymethylene (POM), grade Tenac 2013A used at injection molding of high performance sport products. The injection molding machine employed was an ENGEL, model G/11/10/116/3 and the test pieces were molded at the following different processing temperatures: 180, 190, 200, 210, 220, 230 and 240°C. It was determined that the real in-mold pressure decreases as the processing temperature increases. At the processing temperature of 240°C, decomposition phenomenon occurs by appearance of yellow-brown coloured burns on the surface of the molded parts. The TG analysis performed with a NETZSCH, analizer, model TG 209 proved that POM test pieces molded at 180, 190 and 240°C have the lowest thermal stability due to mechanical degradation and thermal degradation, respectively. For the test pieces molded at 200, 210, 220 and 230°C, the thermal stability modifications of test pieces are totally insignificant compared with the thermal stability of raw material (grains). Concluding the thermal stability is not affected within the processing range of 200 - 230°C. The temperatures determined, T_v and T_t through Differential Scanning Calorimetry (DSC) were accomplished using a DSC calorimeter NETZSCH, type 204 and it was established that the transition temperatures are slightly influenced by the processing temperature and that there are no modifications if compared with the raw grains. The DMA determinations for all test pieces were performed with a NETZSCH analyzer, type 242°C and it revealed that stress frequency has a major influence on the storage modulus (E') and loss tangenta (tan δ) as well. Moreover, the values of E' and tan δ rise as the stress frequency rise, confirming the specialty literature data. Like the TG analysis, the values determined for test pieces molded at 180, 190 and 240°C are different than the values for the pieces molded at other temperatures. The mechanical degradations and thermal degradations are accountable for these modifications.

Based on these experimental results, the recommended processing temperature range is 200 and 230°C.

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