# Study by Thermal Methods of Some Physico-mechanical Properties of Polyamides Used for High Performance Sport Products

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*This paper presents the influence of the processing temperatures on the physico - mechanical properties of polyamides (PA) used in injection molding of high performance sport products. The samples were obtained by processing PA at the following temperatures: 270, 285, 300, 315, 330 and 345°C. It was established that the pressure in the mold decrease as the processing temperature rise. Further, thermal analyses were performed (TG, DSC, and DMA) and it was noticed that the processing temperature had an influence on the thermal stability of the polymer, but the glass transition temperatures ($T_v$) and melt temperatures ($T_t$) were poorly influenced by the processing temperature.*

*Keywords: polyamide, injection molding, TG, DSC, DMA*

The aliphatic polyamides (PA) are linear thermoplastic polymers containing high polar amidic groups, – NH –CO – , separated by flexible hydrocarbonate chains. The amidic groups are involved in strong intermolecular hydrogen bonds so the polymers containing crystalline zones of high density of cohesion energy along with amorphous zones, this providing a certain polymer flexibility. These structural characteristics determine the general properties of aliphatic polyamides, such as: high melting temperature, high breaking strength, high abrasion resistance and high creep resistence, high rigidity and toughness, low dilatation coefficient, low solubility [1]. All these characteristics recommend these polymers to be used for various high performance fields. Most of the aliphatic polyamide production is used for manufacturing of fibres complying with the high tensile strength requirements of this field [2]. Since the price of PA is almost three times higher than the price of general purpose polymers (polyethylene, polystyrene), it is used as plastomer only for items requiring important mechanical characteristics [1].

The main field of technical application of PA is the automotive industry (as body structure, steering wheel, bumper, rearview mirror support for electrical components, etc.) [1]. Also the fiberglass reinforced PA replaced metal in several applications due to its remarkable mechanical properties [1]. The fiberglass reinforced PA triple its tensile strength, considerably and increase rigidity and abrasion resistance, strength at compression, bending and shock, elastic modulus (comparable with metal) and shear strength [3].

Also PA are used in manufacturing of sport items for skating, cycling, water sports, climbing. For example, the speed roller skates have the wheel hubs, rollers frame and the metal skate grip-plate, all made of PA. The PA-thermoplastic elastomer blends permit the obtaining of complex materials as regards toughness [4]. Also fabrics made of PA-polypropylene blends have - if special treated – a high filtration efficiency [6].

In many publications the variation of some physico-mecanical properties depending on the service temperature is analyzed [1, 5].

At injection processing moulding of polymeric materials, the product characteristics are strongly influenced by the temperature and pressure of flowing material at filling the mould cavity. After intrusion of flowing material in mould cavity, there are three stages to be considered for pressure and temperature variation: filling – compacting - solidifying and cooling of melt [7].

The present study aims to determine through thermal analysis methods the variation of some physico-mechanical properties depending on the processing conditions for polyamide 6,6 (grade TECHNYL A 221) used for obtaining of high performance sport products.

**Experimental part**

For obtaining samples, it was used polyamide 6,6 (grade TECHNYL A 221) processed with an injection moulding machine (i.e.,ENGEL, type G/11/10/116/3). The temperature measurement in the flowing material was realized using a thermocouple (i.e., DYNISCO, type Ti422J) fit in the nozzle of injection cylinder in order to get the real temperature within the middle of the melt flow. The following real injection temperatures were set : 270, 285, 300, 315, 330 and 345°C. The cavity pressure was determined using an IDA-type pressure transducer supplied by Dynisco Europe GmbH. For all processing cycles, the injection pressure was set at 1200 bari, injection speed at 20 mm/s, and the temperatures of plasticizing unit (cylinder and nozzle) were set according to the required parameters. Such moulded samples were studied by thermal analysis. In some cases, the determinations were done on raw (unprocessed) granules (pellets) in order to establish a reference for material modification during injection.

The termogravimetric analysis (TG) was performed in nitrogen atmosphere at temperature range of 20 – 990°C and heating rate of 10 K/min, by means of a NETZSCH analyzer (type TG 209 ). The differential scanning calorimetry (DSC) analysis was performed in nitrogen atmosphere at different temperature stages, as follows: heating from 0 to 270°C at a rate of 10 K/min, cooling at -100°C at a rate of 10 K/min, maintaining in isothermal state at -100°C for 5 min, heating at 400°C

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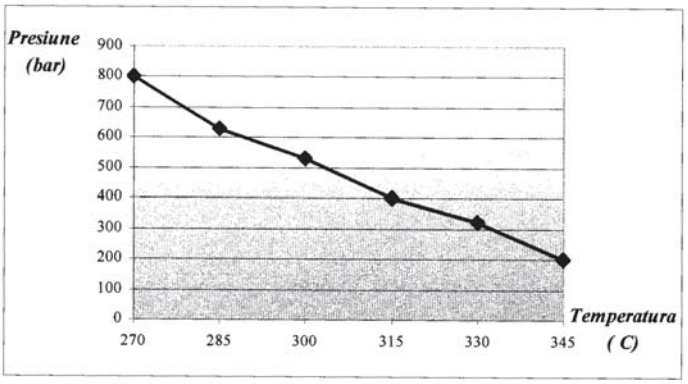


Fig.1. The dependence on real injection temperature of peak pressure for PA (grade TECHNYL A 221)

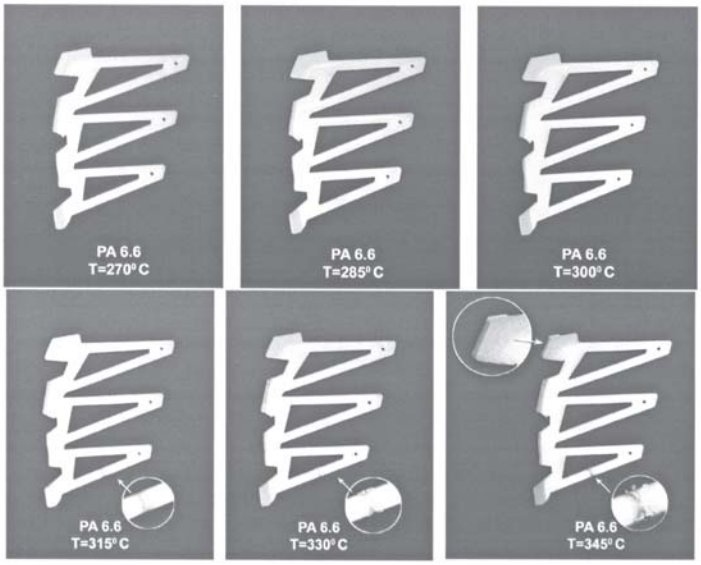


Fig.2. The influence of injection temperature on quality of moulded parts (polymer : PA.grade TECHNYL A 221)

at a rate of 5 K/min.The instrument employed was a Differential Scanning Calorimeter (i.e.,NETZSCH,type DSC 204). The dynamic mechanical analysis (DMA) was performed in air, as follows: temperature range 0 – 200°C, heating rate 1 K/min, strain frecquencies 0.5; 1; 2; 5; and 10 Hz. The dynamic mechanical analyzer (i.e.,NETZSCH, type DMA 242 C) was used in a dual cantilever bending mode.

**Results and argumentation**

For the six stages of processing temperature it was determined that if the injection parameters were maintained constant, the real mould pressure decreased from 800 bar (at processing temperature of 270°C) to 200 bari (at processing temperature of 345°C) (fig. 1). This result is accountable to the strong decrease in viscosity of melted polymer.

In figure 2 there are presented the parts injection molded at six different processing temperatures. It is noticed that the parts processed at temperature of 270ºC, 285ºC and 300ºC are quality-compliant since the mould cavity is fully filled and there are no apparent flow marks, material shrinkage or degradation.The material thermal degradation occurs to the parts moulded at the next three processing temperatures (315, 330 and 345ºC), being especially prominent at the 345ºC processing. Out of these remarks, it results that and the optimum processing temperature ranges between 270 and 300ºC since above this limit it occurs thermal degradation burrs.

Figure 3 presents the TG diagram for PA processed at 285°C and the table 1 presents the inflexion points on TG diagram, as well as the mass loss implied at temperatures of 200, 300, 400, 500 and 600°C.

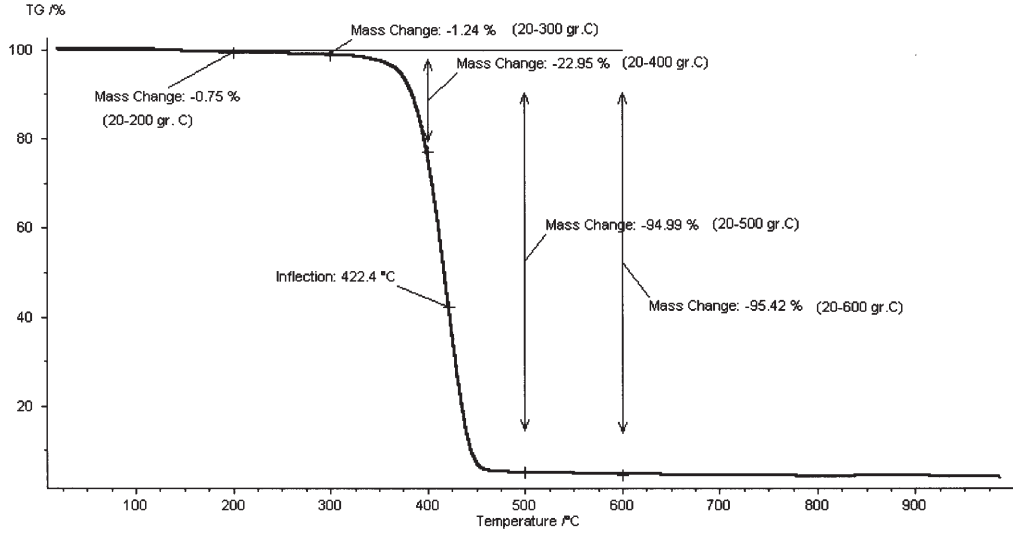


Fig. 3. TG diagram for PA sample processed at 285ºC

**Table 1**
MASS LOSS FOR PA PROCESSED AT DIFFERENT TEMPERATURES

| Processing temperature of PA [°C] | Inflexion [°C] | Mass loss [%] at temperature of [°C] | | | | |
|---|---|---|---|---|---|---|
| | | 200 | 300 | 400 | 500 | 600 |
| granules | 425,1 | 0,57 | 0,87 | 20,46 | 94,97 | 95,50 |
| 270 | 408,5 | 2,33 | 2,79 | 45,81 | 96,87 | 96,96 |
| 285 | 422,4 | 0,75 | 1,24 | 22,95 | 94,99 | 95,42 |
| 300 | 422,0 | 0,92 | 1,38 | 21,75 | 95,34 | 95,83 |
| 315 | 421,8 | 1,08 | 1,48 | 24,13 | 95,82 | 96,07 |
| 330 | 425,8 | 0,69 | 1,00 | 20,10 | 94,04 | 94,50 |
| 345 | 411,5 | 2,28 | 2,72 | 41,82 | 96,97 | 97,07 |

The inflexion point in TG diagram represents the temperature at which the decomposition velocity is maximum. From table 1 it results that the lowest values of inflexion points are correspondent to the polymer processed at 270°C and 345°C, respectively. This fact is accountable as follows: processing at 270°C, the melt viscosity is still too low favouring mechanical degradation of material, since thermal degradation is present at 345°C processing. For granules and for samples processed at other temperatures, the inflexion points have close values. Same observation is valid for mass losses within temperatures of 200, 300 and 400°C, respectively. Taking into account the previous observations and figure 2, the conclusion is that the best results are obtained by processing at 285 and 300°C.

In table 2 there are presented the values for glass transition temperature $T_v$ (the inflexion point on DSC curve) and melting temperature $T_t$ (endothermal peak on DSC curve) as function of processing temperature.

It is noticeable that $T_v$ varies from 59.6 to 60.6°C, and $T_t$ varies from 261.1 to 262°C, so that the modifications are unimportant, these results being similar to the measurements on raw (unprocessed) granules. In conclusion, the processing temperature do not influence the transition temperatures of polyamide 6.6 (grade Technyl A 221).

The DMA determinations for all samples establish that stress frequency have a major influence both on storage modulus (E') and loss tangenta (tan δ). În table 3 are presented the values for E' at temperature of 0°C, as a function of stress frequency and processing temperature .

**Table 2**
GLASS TRANSITION TEMPERATURE $T_v$, AND MELTING TEMPERATURE $T_t$ FOR PA PROCESSED AT DIFFERENT TEMPERATURES

| Processing temperature of PA [°C] | $T_v$ [°C] | $T_t$ [°C] |
|---|---|---|
| Granules | 60,2 | 262,0 |
| 270 | 59,9 | 261,3 |
| 285 | 60,4 | 261,1 |
| 300 | 59,6 | 261,3 |
| 315 | 60,1 | 261,6 |
| 330 | 60,2 | 261,3 |
| 345 | 60,6 | 261,1 |

It is noticeable from table 3 that the stress frequency influences the storage modulus value - as E' increases with stress frequency - and the results are concordant with the theory related to temperature – time analogy

**Table 3**
VALUES OF E' AT 0°C FUNCTION OF STRESS FREQUENCY AND PROCESSING TEMPERATURE

| Stress frequency [Hz] | Values of E' [MPa] for processing temperature [°C] | | | | | |
|---|---|---|---|---|---|---|
| | 270 | 285 | 300 | 315 | 330 | 345 |
| 10 | 980 | 880 | 880 | 920 | 930 | 990 |
| 5 | 970 | 870 | 870 | 910 | 925 | 980 |
| 2 | 960 | 860 | 860 | 900 | 915 | 970 |
| 1 | 950 | 850 | 850 | 890 | 905 | 955 |
| 0,5 | 940 | 845 | 840 | 880 | 890 | 950 |

**Table 4**
VALUES OF TAN δ FUNCTION OF STRESS FREQUENCY AND PROCESSING TEMPERATURE

| Stress frequency [Hz] | Values of peak tan δ,[°C] for processing temperature [°C] | | | | | |
|---|---|---|---|---|---|---|
| | 270 | 285 | 300 | 315 | 330 | 345 |
| 10 | 45,9 | 48,9 | 48,2 | 47,6 | 47,3 | 47,0 |
| 5 | 45,3 | 48,3 | 49,0 | 47,6 | 47,2 | 46,8 |
| 2 | 45,5 | 47,2 | 48,6 | 47,8 | 47,4 | 47,4 |
| 1 | 45,0 | 48,4 | 47,9 | 47,5 | 47,4 | 47,4 |
| 0,5 | 45,3 | 47,1 | 50,1 | 47,8 | 47,6 | 47,7 |

[8,9]. According to this theory elaborated by M.L. Williams, R.F. Landel and J.D. Ferry, at increasing the frequency of actuating force, the fluctuation network has no time to react and the material is behaving as if the determination temperature would be lower (for the initial stress frecuency).

From table 3 it can be seen also that the processing temperature has a major influence on E'. The values for processing at 270 and 345 °C are different from the ones for the others processings, but these are concordant with the results determined by TG analysis, which confirms that mechanical and thermal degradations occur in material at these temperatures.

The results for peak of tan δ values that can be assimilated with glass transition temperature - are shown in table 4.

The values for glass transition temperature are slightly influenced by the processing temperature and the stress frequency, besides the same conclusions were established at the DSC analysis too. The differences between glass transition temperatures determined using DSC and DMA analyses are due to different methods of determination and different heating rates.

## Conclusions

We have studied the modification of physico-mechanical properties for polyamide 6.6 resin (grade TECHNYL A 221) at injection moulding of high performance sport products using an ENGEL machine, type G/11/10/116/3. For this purpose, samples were moulded at different processing temperatures (270, 285, 300, 315, 330 and 345°C). It was determined that the real mould pressure decreases as the processing temperature increases. At processing temperatures over 300°C, material degradation arises and becomes significant at 345°C. The TG, analysis performed with a NETZSCH instrument (type TG 209 ) proves that PA in 270 and 345°C moulded samples has the lowest thermal stability due to mechanical degradation and thermal degradation, respectively while the thermal stability modification is insignificant for samples moulded at other temperatures, comparative with the one of raw (unprocessed) granules. In conclusion, the thermal stability is not affected within the processing range of 285 - 330°C.

The glass transition and melt temperatures -$T_v$ and $T_t$ – determined through Differential Scanning Calorimetry (DSC) method using a NETZSCH instrument (type DSC 204) proved that the transition temperatures are poorly influenced by the processing temperature and there is no modification comparative with raw granules. It was determined through DMA analyses by using a NETZSCH instrument (type DMA 242 C) that the stress frequency has a major influence on storage modulus (E' and a less significant influence on loss tangenta (tan δ). The values of E' increase with stress frequency, in accordance with the specialty literature data. Like the TG analysis, the values determined for samples moulded at 270 and 345°C are different from the values of samples processed at other temperatures. These modifications can be attributed to mechanical and thermal degradation. From these results, the recommended processing temperatures ranges between 285 and 300°C .

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