Thermal Analysis of Some Mechanical and Physical Properties of Thermoplastic Polyurethanes Used in Manufacturing of Performance Sport Products

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This paper presents the influence of processing temperature on the mechanical-physical properties of thermoplastic polyurethanes (TPU) used at injection moulding of performance sport products. The test-pieces were moulded at the following real injection temperatures : 200°C, 210°C, 220°C, 230°C and 240°C. It was determined that the in-mould pressure decreased with increasing of the processing temperature. Also the following thermal analysis were performed : Thermogravimetry (TG), Differential Scanning Calorimetry (DSC) and Dynamic-Mechanical Analysis (DMA). It was established that the processing temperature has a significant influence on the thermal stability and on the glass transition temperature of polymer while the flow temperature is slightly influenced by the processing temperature.

Keywords: thermoplastic polyurethane (TPU), injection moulding, Thermogravimetry (TG), Differential Scanning Calorimetry (DSC) , Dynamic-Mechanical Analysis (DMA)

The thermoplastic polyurethanes (TPU_S) are polymers used more frequently for manufacturing of various products in automotives, electrotechnics and sport equipment industry. TPU_S are obtained by reaction of diisocyanates and difunctional polyols [1]. The polyols can be long-chain diols and short-chain diols. The result of the polyaddition reaction between three components - diisocyanate, long-chain diols and short-chain diols- is the linear polyurethane. The long-chain diols are the flexible segment of the polyurethane while the combination between the diisocyanate and the short-chain diol represents the hard segment of polyurethane (fig.1).

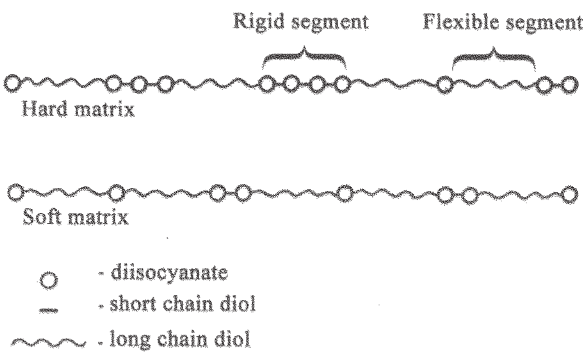

Fig.1 Structure of thermoplastic polyurethane (TPU) [2]

The properties of TPU depend on the nature and proportion of the initial components and on the reaction conditions. Moreover, the types of polyols used in production of polyurethane have a great influence on the properties of the resulted polyurethane. There are two types of polyols which can be used for production of polyurethane: polyesters and polyethers with terminal groups –OH.

The polyester-diol based TPU_S have a remarkable high mechanical and thermal strength combined with high resistance to mineral oil and hydraulic fluids. However, if TPU_S are used in severe wet conditions, their major disadvantage occurs and must be considered: TPU_S have a tendency for hydrolysis implying the decrease of their mechanical strength.

The polyether-diol based TPU_S have a higher resistance to hydrolysis, a better flexibility at low temperatures and resistance against microbiological degradation.

All the polyurethane grades contain different additives as well in order to increase their processability or improve specific properties. Thus, the fiber glass reinforcement leads to an increase of rigidity and 5-30% additional content of mica leads to improvement of mechanical properties (increase of hardness and of frictional resistance) of polyurethane [3].

The TPU_S are used for manufacturing of:

- technical automotive parts (e.g., front masks, sealing rings, grills, rocker panels, protection boots, snow anti-skid chains, protection rings for tie rod ends) ;
- electrotechnical and householding appliance accesories (e.g., protective coating for different sorts of cables - electric and telephone cables, cables for seismic recordings, etc.), plugs and sockets, different sorts of hoses (e.g., hoses for conveyance of abrasive materials, for vacuum cleaners, for pneumatic circuits, etc.), housing for drilling machines, conveyor belts, bearing cages, various types of rollers, etc.;
- different sport equipment (e.g., ski boots, roller skates boots, bindings for snow rockets, soles for sport shoes, snowboard boots, protective caps for ski tips), etc. [4 - 7].

At injection moulding of TPU_S two parameters - temperature and pressure - of the flowing-state material at filling the mould cavity are determinant for the characteristics of the moulded products.

This paper presents the variation of some mechanical-physical properties of TPU depending on the processing conditions. The results were obtained through thermal analysis methods applied to the TPU grade Desmopan KA 8377 used for manufacturing of performance sport items.

Experimental part

The test pieces were moulded in TPU, grade Desmopan KA 8377 using an injection moulding machine ENGEL, model G/11/10/116/3. The temperature of the flowing-state material was measured with a thermocouple DYNISCO,

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type Ti422J which was fit in a special port of 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: 200, 210, 220, 230 and 240°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 at 1600 bar, injection speed at 20 mm/s and the temperatures of plasticizing cylinder and of cylinder nozzle were set accordingly. The moulded test pieces were examined through thermal analysis. Also for comparison purpose, raw polymer grains were used in order to determine the material alterations during injection.

The thermogravimetry (TG) analysis was carried out using a NETZSCH analyzer, typeTG 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 to 200°C, with a rate of 10 K/min, cooling at -100°C with a rate of 10 K/min, isothermal regime 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 - 50 and + 150°C, heating rate of 1K/min, stress frecquency of 0,5; 1; 2; 5; and 10 Hz .

Results and discussion

If the injection parameters were maintained constant for all the five stages of processing temperatures (200, 210, 220, 230 and 240°C) it was determined that the real in-mould pressure decreases from 1400 bar for processing at 200°C to only 400 bar for processing at 240°C (fig. 2). This fact is explained by the major decrease in viscosity of the polymer melt.

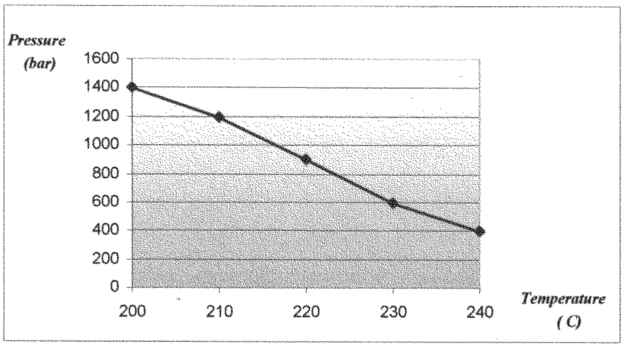

Fig.2. Dependence of in-mould pressure peak on the real injection temperature for TPU (Desmopan grade KA 8377)

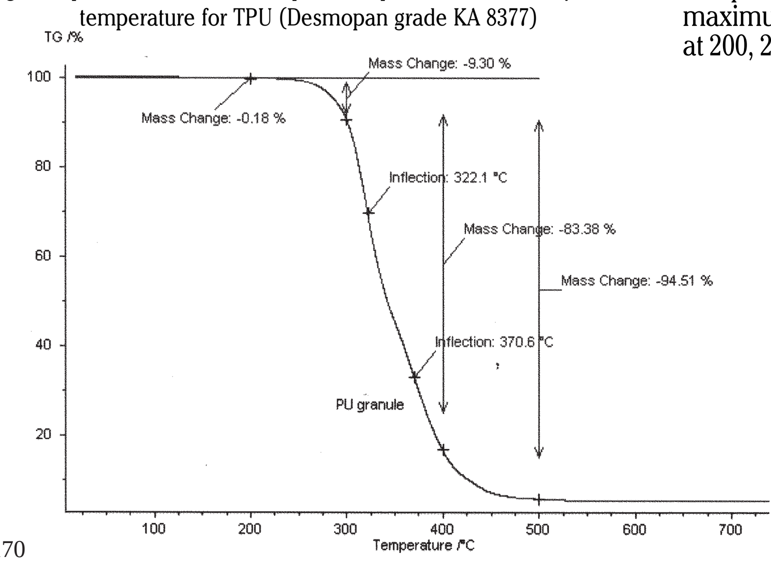

Fig.4. TG diagram for TPU grains

The pieces moulded at five processing temperatures are presented in figure 3. With reference to the quality of moulded pieces, it can be remarked that quality is inadequate if processing temperature is too low (200 and 210°C) or too high (240°C). On the one hand, at 200 and 210°C, the pieces are incompletely contoured and on the other hand, the surface of the piece moulded at 240°C has visible marks of polymer's thermal degradation. Only the pieces moulded at 220°C and 230°C have an adequate quality since the mould cavity was completely filled, the surface of piece is free of melt flow marks or shrinkage and no degradation of polymer occured. As a conclusion of these observations: the optimal processing temperature is ranging between 220 and 230°C.

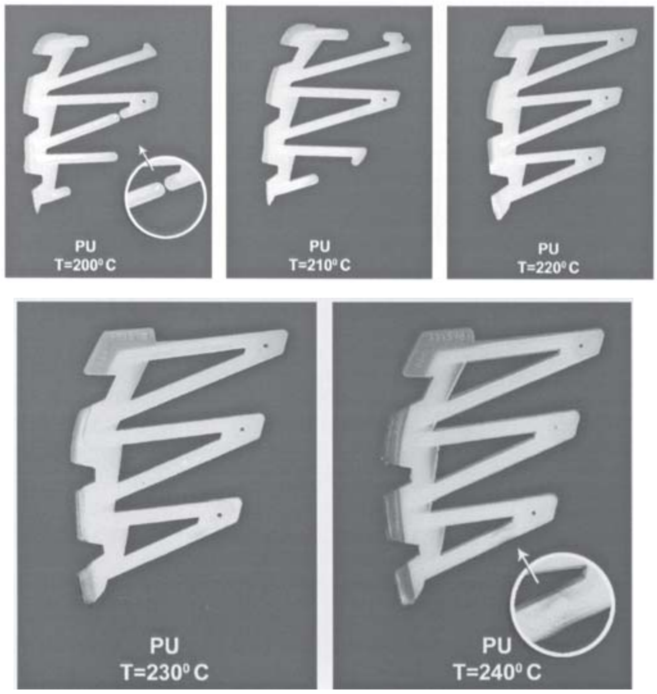

Fig.3. Influence of injection temperature on the quality of TPU moulded parts (grade Desmopan KA 8377)

In figure 4 is represented the TG diagram for TPU grains and in table 1 are presented the inflection points on TG diagram, and the mass losses at 200, 300, 400 and 500°C.

The TG diagram has two inflection points (322.1 and 370.6°C), one is due to the decomposition of the urethane group and the other is due to the decomposition of the esteric group of the polyol used at polyurethane synthesis. The inflection points on TG diagram represent the temperatures where the decomposition rate has a maximum. In table 1. it can be noticed that processing PU at 200, 210 and 240°C favourize reaching the lowest values

Table 1
MASS LOSSES FOR TPU PROCESSED AT DIFFERENT TEMPERATURES

Processing temperature of TPU [°C]	Inflection 1 [°C]	Inflection 2 [°C]	Mass loss [%] at temperature of [°C]			
			200	300	400	500
grains	322.1	370.6	0.18	9.30	83.38	94.51
200	321.1	366.3	0.19	11.04	83.75	94.10
210	321.2	366.7	0.186	10.60	83.40	94.00
220	321.9	370.1	0.182	9.40	83.10	93.90
230	322.0	370.3	0.181	9.35	83.00	93.90
240	319.3	366.9	0.19	10.78	82.06	93.59

Table 2
THE GLASS TRANSITION TEMPERATURE AND FLOW TEMPERATURE FOR TPU PROCESSED AT DIFFERENT TEMPERATURES

Processing temperature of TPU [°C]	T_v [°C]	T_c [°C]
Grains	56.2	207.4
200	56.5	206.4
210	57.0	206.6
220	57.8	204.4
230	58.7	205.5
240	59.8	205.5

Table 3
VALUES OF STORAGE MODULUS (E') AT - 50°C RELATIVE TO DIFFERENT STRESS FREQUENCIES AND PROCESSING TEMPERATURES

Stress frequency [Hz]	Value of E` [MPa] at specific processing temperature [°C]				
	200	210	220	230	240
10	1150	1140	1000	1000	1120
5	1130	1120	990	990	1110
2	1120	1110	980	980	1100
1	1100	1100	970	970	1090
0,5	1080	1080	960	960	1085

of the inflection points. This fact can be explained by degradation of polymer: by mechanical degradation as the result of a too low melt viscosity at 200 and 210°C processings and by thermal degradation which occurs at 240°C processing. For raw material grains and for processings at other temperatures, the values of inflection points are similarly close. The same observation is valid for mass losses occured till 200 and 300°C. Considering the previous observations and the diagram presented in figure 3, the conclusion is that the best results are obtained for processing between 220 and 230°C.

In table 2 are presented the values for glass transition temperature T_v and flow temperature T_c (the endotherm peak on the DSC curve) depending on the processing temperatures.

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

The DMA determinations establish for all test pieces that stress frequency have a major influence on the storage modulus (E'). In table 3 are presented the values of storage modulus (E') measured at - 50°C relative to different stress frequencies and processing temperatures.

It can be remarked from table 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 [8,9]. According to [9] 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 the mentioning of the initial stress frequency).

From table 3 it can be noticed that E' is largely influenced by the processing temperature, and that the values determined at 200, 210 and 240°C are different than the values attached to other processing temperatures. However, these determinations are concordant with the results obtained through TG analysis and confirming that the material is mechanically degraded at 200, 210°C, respectively thermally degraded at 240°C.

Conclusions

It was studied the modification of physical-mechanical properties for thermoplastic polyurethanes (grade Desmopan KA 8377) used at injection moulding of high performance sport products (e.g., ski boots, bindings for snowboard, protective caps for ski tips) destined to be used at low temperature environmental conditions. The injection moulding machine employed was an ENGEL, model G/11/10/116/3 and the test pieces were moulded at the following processing temperatures: 200, 210, 220, 230 and 240°C. It was determined that the real in-mould cavity pressure decreases with increasing of the processing temperature. Also it was determined that the test pieces are not completely moulded (incompletely contoured) at 200 and 210°C, while thermal degradation marks are visible on the surface of the test pieces moulded at 240°C. The TG analysis performed with a NETZSCH, analizer, type TG 209 proved that TPU test pieces processed at 200, 210 and 240°C have the lowest thermal stability due to mechanical degradation and thermal degradation, respectively. For the test pieces processed at 220 and 230°C, the alteration of thermal stability is totally insignificant if compared with the thermal stability of raw material (grains). Concluding, the thermal stability is not affected within processing temperature range of 220 - 230°C.

The Differential Scanning Calorimetry (DSC) determinations of the flow temperature T_c were accomplished using a DSC calorimeter NETZSCH, type 204. It was established that the flow temperature T_c is slightly influenced by the processing temperature. Also the increase of processing temperature leads to a slight increase of glass transition temperature.

The Dynamic-Mechanical Analysis (DMA) performed using a NETZSCH analyzer, type 242 C revealed that the stress frequency has 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. Very similar to TG analysis, the values determined for test pieces moulded at 200, 210 and 240°C are different than the values for the pieces moulded at 220 and 230°C. The mechanical degradations and thermal degradations are accountable for these modifications. Based on these experimental results, 220 and 230°C is recommended as the optimal processing temperature range.

This paper represents a new advanced study concerning the materials used for the manufacturing of the performance sport products [10-12].

Bibliography

1. TROTIGNON, J., P., VERDU, J., DOBRACGINSKY, A., PIPERAUD, M., Matieres Plastiques. Structures-proprietes, Mise en oeuvre, Normalisation, Editions Nathan, Paris, 1996, p.126

2. MĂRIEŞ, Gh., R., E., MANOVICIU, V., MANOVICIU, I., Consideraţii privind utilizarea PU în articole sportive de performanţă, Analele Universităţii din Oradea, Fascicula Arte Vizuale, 2, Editura Universităţii din Oradea, 2005, p.125

3. PINTO, U., A., VISCONTE, L., L., Y., NUNES, R., C., R., Mechanical properties of thermoplastic polyurethane elastomers with mica and aluminium trihydrate, European Polymer Journal 37 (9):: 1935-1937, 09, 2001

4. BEYER, M., LOHMAR, J., Schon und robust, Kunststoffe, 1, 2000, p.98

5. SALM, W., Nur Fliegen ist Schoner, TPU in neuen Kombinationen fur Sport und Spiel, Kunststoffe, 7, 1999, p.118

6. SCHOLL, A., PIRODDI, A., Sicher und Gerauschdampfend, Kunststoffe, 4, 1998, p.556

7. MANOVICIU, V., MĂRIEŞ, Gh., R., E., Materiale compozite cu matrice organică, Editura Universităţii din Oradea, Oradea, 2005, p.152

8. KULEZNEV V.N., SHERSHNEV V.A., The Chemistry and Physics of Polymers, Mir Publishers, Moscow, 1990, p. 146

9. WILLIAMS M.L., LANDEL R.F., FERRY J.D., J. Am. Chem.Soc., **77**, 1955, p. 3701

10. MĂRIEŞ, R.E., MANOVICIU, I., BANDUR, G:, RUSU, G., PODE, V:, Mat. PLast., **44**, nr. 4, 2007, p. 289

11. MĂRIEŞ, R.E., MANOVICIU, I., BANDUR, G., RUSU, G., PODE, V., Mat. Plast., **45**, nr. 1, 2008, p. 3

12. MĂRIEŞ, Gh.R.E., MANOVICIU, I., BANDUR, G., RUSU, G., PODE, V., Mat. Plast., **46**, nr. 1, 2009, p. 58

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