Study by Thermal Methods of Physico-Mechanical Properties of Polycarbonate used for High Performance Sport Products

RADU EMIL MĂRIE [a1], IONEL MANOVICIU[2], GEZA BANDUR[2*], GERLINDE RUSU[2], VASILE PODE[2]
[1]University of Oradea, Faculty of Visual Arts , 39 Independentei Str., 410067, Oradea, Romania
[2]University Politehnica University of Timi°oara, 2 P-þa Victoriei, 300006, Timisoara, Romania

This paper presents the influence of the processing temperatures on the physico – mechanical properties of PC used in injection molding of high performance sport products. The samples (test-pieces) were obtained by processing PC at the following temperatures: 280°C, 295°C, 310°C, 325°C and 340°C. It was established that the pressure in the mold decreases as the processing temperature rises. 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 and on the activation energy (E_a) of the glass transition phase, but the glass transition temperatures T_g were slightly influenced by the processing temperature.

Keywords: polycarbonate, injection molding, TG, DSC, DMA

Polycarbonate (PC) is one of the thermoplastic polymers with a wide range of applications due to its excellent physico-chemical properties , such as: transparency, high deformation temperature, high mechanical strength , good thermal stability [1]. For this reason, the polymer is used for high performance sport items,as straps and buckles for skate boots and ski boots, lenses for sport safety glasses,etc.

It is well known that the stress-deformation diagram for amorphous polymers , states a temperature dependance of the deformation velocity.For several polymers, a transition threshold between deformation velocity and temperature, was identified above which this significantly increases [2]. Taking into account these considerations, several studies were realized referring to temperature dependent modification of PC properties.

It was studied the thermal degradation of PC in helium atmosphere using the TGA/FTIR, GC/MS and LC/MS technics and it was determined that the degradation is mainly the result of chain break in the isopropyliden, hydrolise/alcoholise and rearrangement of carbonat groups [3]. The thermal degradation occurs as the result of succesive reactions [3-6]. In the first stage of pyrolysis, in a 400-500°C temperature range,it takes place intermolecular exchange reactions resulting cyclical products and hydrolisis reactions generating fenolic terminal group and CO_2.

For the purpose of studying different PC physical–mechanical properties, Dynamic Mechanical Analyses (DMA) were performed for a wide range of temperature (from -140 to 180°C) and different strain frequencies. Thus the PC viscoelastic features were characterized for a wide range of deformation velocities and temperatures [7,8].

At injection moulding of polymeric materials,the product characteristics are strongly influenced by the temperature and pressure of flowing-state material filling the mould cavity.Beginning with the intrusion,there are three stages to be considered (filling – compacting - solidifying and cooling of melt [9]) for the pressure and temperature variation. The present study aims to determine by thermal analysis methods the alteration of some polymer properties depending on the real injection temperature

Experimental part

For obtaining samples,it was used polycarbonate (grade XANTAR 18 UR) processed by 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: 280°C, 295°C, 310°C, 325°C and 340°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 1600 bar, injection speed at 25 mm/s, and the plasticizing unit (cylinder and nozzle) temperatures were set according to the required parameters. Such moulded samples were studied by thermal analysis.

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 (TG 209 type).

The differential scanning calorimetry (DSC) analysis was performed in nitrogen atmosphere at different temperature stages,as follows : heating from 0 to 280°C at a rate of 10 K/min, cooling at 0°C at a rate of 10 K/min, maintaining in isothermal state at 0°C for 5 min, heating at 400°C 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 at temperature range 20 – 180°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 five stages of processing temperature it was determined that if the injection parameters were maintained constant,the real mould pressure decreased as temperature rised (fig. 1).

On the other hand,it was determined that a too low injection temperature (i.e.,280°C) leads to parts with visible surface flow marks – meaning that the forming

* *email: maries.radu@rdslink.ro; Tel.: (+40) 0359 43 63 77*

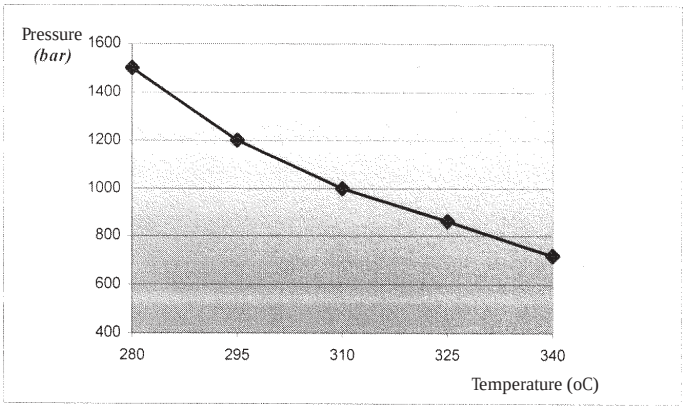

Fig. 1. The dependence of pressure peak on the real injection temperature
(polymer : PC, type Xantar 18 UR)

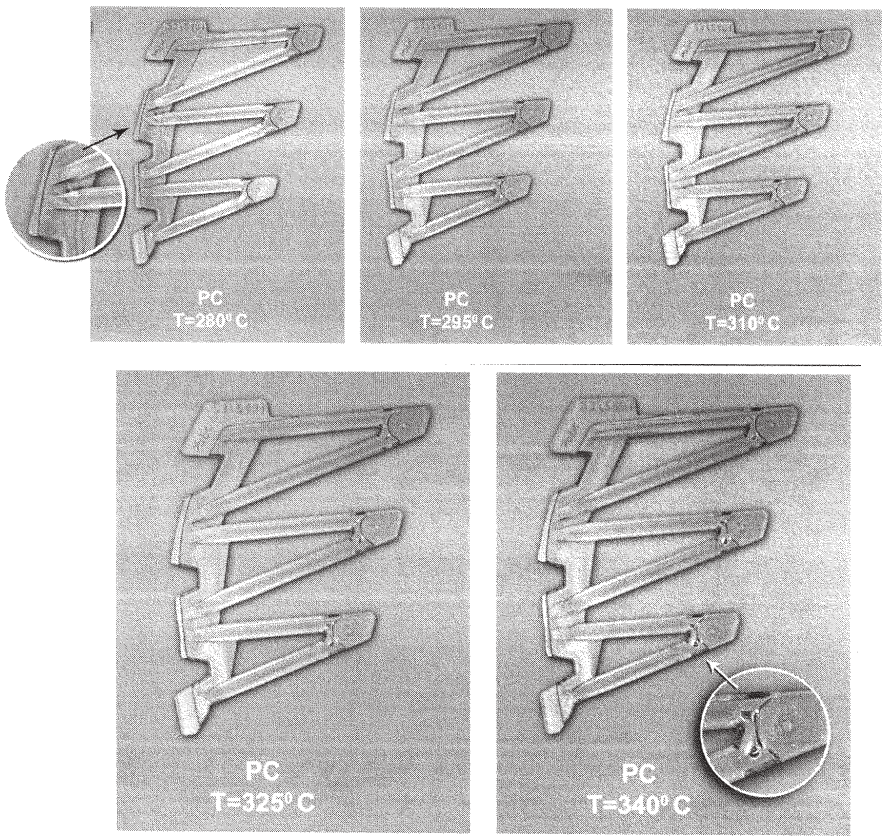

Fig. 2. The influence of the injection temperature on the quality of injection moulded parts (polymer : PC ,type Xantar 18 UR)

temperature is too low and the material is not completely homogenized in the plasticizing unit (injection cylinder) - and a too high injection temperature (i.e.,340°C) leads to incipent material degradation (fig. 2).

The TG analysis showed that the thermal stability of polymer was diminished upon processing. On TG diagram the inflexion points are as follows : at 499°C for PC granules, at 482,4°C for samples processed at 280°C and for all the other samples the point lies within 489.2°C - 493.3°C.

In figure 3 there are presented the TG diagrams for PC granules and for samples processed at 280°C, 310°C and 325°C. The inflection points on the TG diagram are at 490,5°C (processing at 295°C) and 490,7°C (processing at 340°C).

The inflection point on the TG diagram indicates the limit where the speed of the process (i.e.,degradation) is maximum. Decrease of temperature for inflexion in TG curve must be referred to the decrease of molecular mass during processing The greatest decrease occurs on processing at 280°C when the polymer flow-state is uncompletely reached,this generating thermal and mechanical degradation.

At higher temperatures – cause of decrease in material viscosity – the thermal degradation are preponderant.

On table 1 there are presented the mass loss determinations through TG analysis within 200, 300, 400, 500 and 600°C temperature.

The results presented in table 1 confirm that below 500°C raw material (granules) has the highest (best) thermal stability and that the samples processed at 280°C have the lowest thermal stability .

The DSC analysis proved the very low variation of glass transition temperature (T_g) function of processing temperature.There is a slight difference between the raw granules having T_g = 145,3°C (according to the inflexion point in the DSC diagram) and the processed samples,where T_g ranges between 140,0 and 140,8°C. T_g is 140,5°C. for samples processed at temperature 280 and 310°C, respectively.

In figure 4 are presented the DSC diagrams for PC granules and for samples processed at 295, 325 and 340°C.

The decrease of glass transition temperature of samples compared with granules is the result of material

Table 1

MASS LOSS FOR PC PROCESSED AT DIFFERENT TEMPERATURES

Processing temperature of PC [°C]	Mass loss [%] at temperature of [°C]				
	200	300	400	500	600
grains	0.01	0.01	0.26	45.93	73.60
280	0.03	0.03	1.87	69.57	76.45
295	0.01	0.02	1.75	64.16	76.45
310	0.01	0.02	1.76	58.99	75.90
325	0.01	0.11	1.74	64.15	76.85
340	0.01	0.14	0.90	62.43	74.22

Table 2

TEMPERATURE VARIATION AT WHICH THE STORAGE MODULUS TURNS TO DECREASE AND THE TEMPERATURE PEAK OF TAN δ FOR PC PROCESSED AT 325°C

Stress frequency [Hz]	Onset temperature for E′ [°C]	Temperature peak of tan δ [°C]
10	138.8	153.6
5	137.9	152.6
2	136.3	150.3
1	135.5	149.2
0,5	134.3	147.5

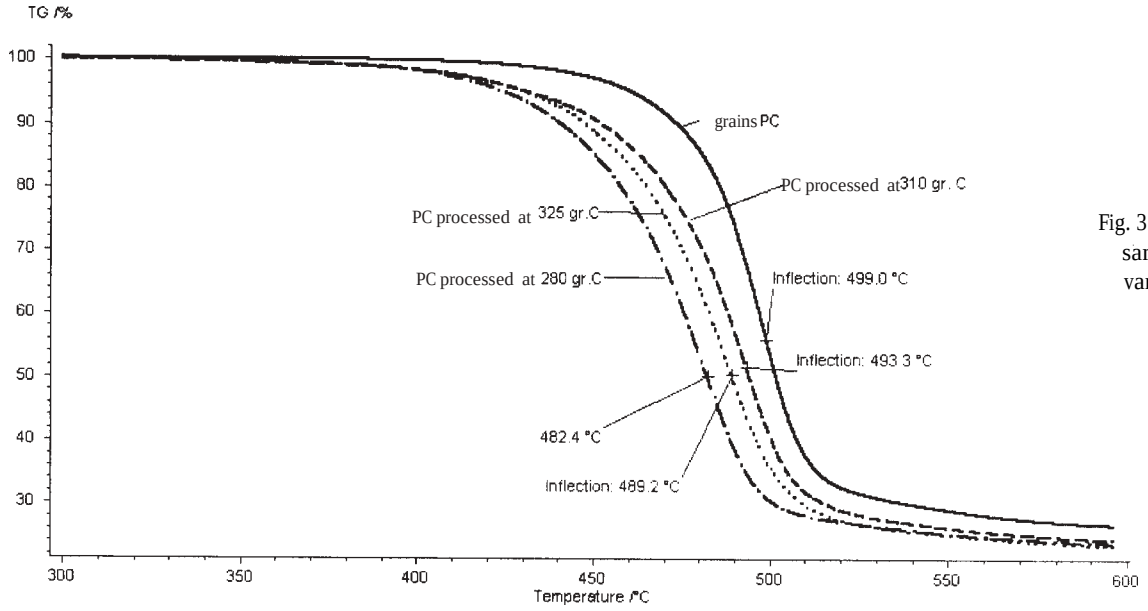

Fig. 3. TG Diagrams for PC samples processed at various temperatures

degradation due - the most likely - to the improper material drying prior processing as the remaining water content leads to macromolecular chain splitting,molar mass decrease and the glass transition temperature decrease consequently.

The DMA determinations for all the samples establish that the stress frequency has a major influence both on storage modulus (E') and on loss tangenta (tan δ). For example, in table 2 are presented the temperatures as a function of stress frequency : temperature at which the storage modulus turns to decrease (onset temperature)

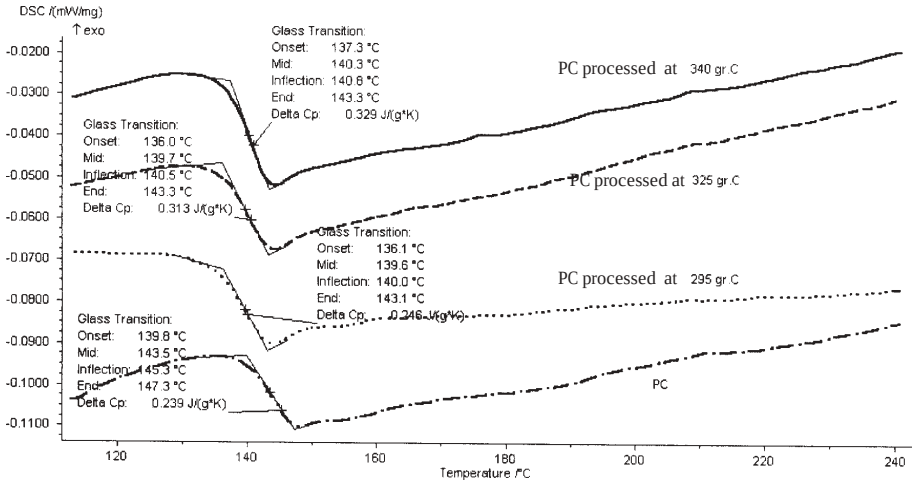

Fig. 4. DSC Diagrams for PC samples

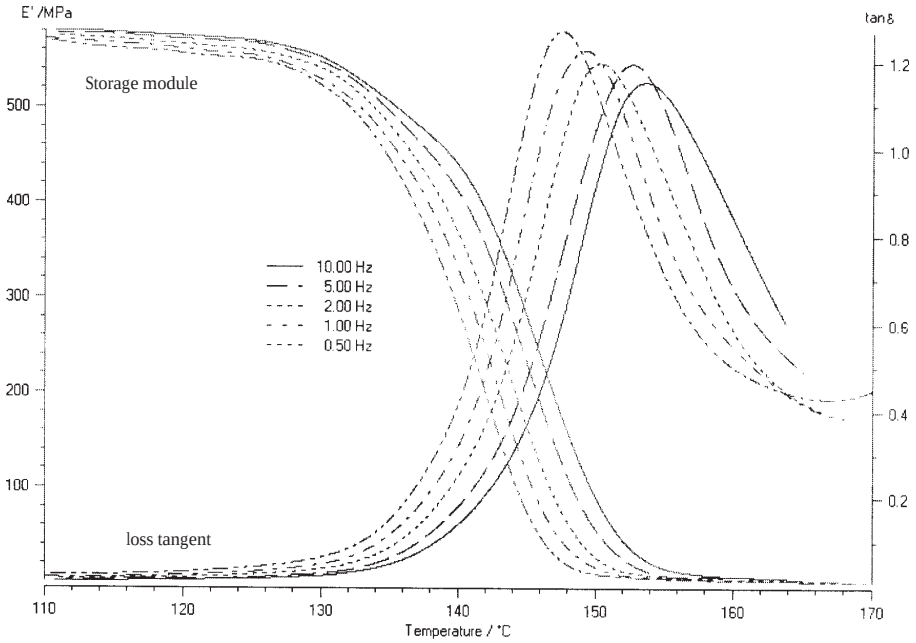

Fig. 5. DMA Diagrams for PC processed at 325°C

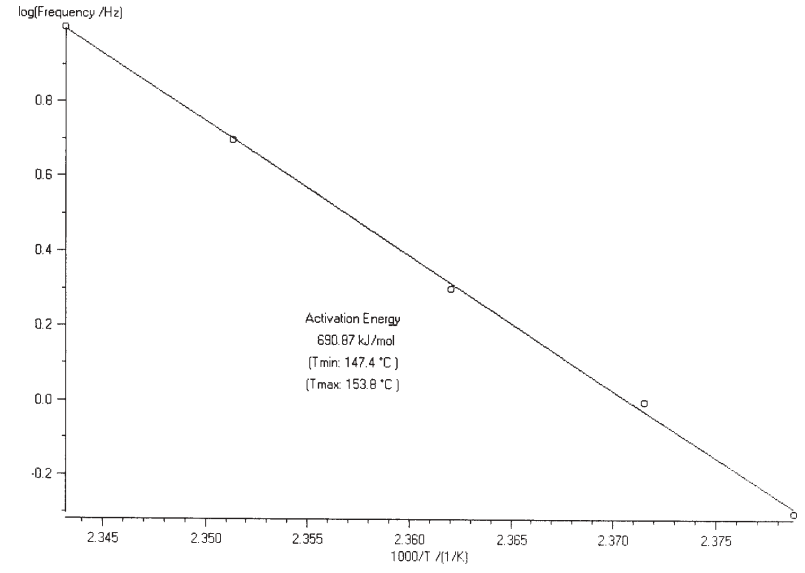

Fig. 6. The calculation diagram for E_a to glass transition of PC processed at 280°C

and the temperature peak of tan δ for PC processed at 325°C, in figure 5, are presented the correspondent diagrams.

The results presented in table 2 and figure 5 are according to the data provided by specialty literature [10,11] referring to temperature-time analogy .

The temperature peak of tan δ can be assimilated with the glass transition temperature [10] and the activation energy (E_a) of this transition can be calculated upon the values obtained - using the DMA-Analysis software - for different stress frequency.

In figure 6 is presented a calculation example for E_a at glass transition of PC processed at 280°C, and table 3 presents for all the samples of the glass transition temperature values, T_g, and the activation energy of glass transition E_a, table 3 shows that increasing of stress frequency at DMA ,the glass transition temperatures become higher, according the data provided by the

Table 3

GlASS TRANSITION TEMPERATURES OF PC SAMPLES – AS A DMA METHOD DETERMINATION - RELATED TO DIFFERENT STRESS FREQUENCY, AND THE ACTIVATION ENERGY OF GLASS TRANSITION PROCESS

Processing temperature [°C]	Glass transition temperature [°C] vs. Stress frequency [Hz]					Activation energy [kJ/mol]
	10	5	2	1	0,5	
280	153.8	152.3	150.4	148.7	147.4	690.87
295	155.0	153.1	151.5	149.7	148.3	674.38
310	153.4	152.3	150.2	148.6	147.4	713.80
325	153.6	152.6	150.3	149.2	147.5	718.72
340	159.0	157.6	155.5	154.4	152.6	727.98

specialty literature [10]. The values for T_g determined through DMA method are higher than theones obtained through DSC method - but still in accordance with the literature data - difference due to the use of a different determination modality.

Glass transition temperatures are slightly influenced by the processing temperature,as it was noticed at the DSC determination as well. Only the 340°C processed samples have a slight rise of T_g, but at this temperature material degradation phenomena occur (fig. 2) what induce the macroradical formation and recombination leading to alteration of physico-mechanical properties.

The activation energy of the glass transition increases as the processing temperature increases, excepting the 280 °C processed sample,but mechanical degradation must be considered in this case.

Conclusions

We have studied the modification of physico-mechanical properties for polycarbonate resin (grade XANTAR 18UR) at injection moulding of high performance sport products using an, type G/11/10/116/3 ENGEL machine. For this purpose, samples were moulded at different processing temperatures (280, 295, 310, 325 and 340°C).

It was determined that the real mould pressure decreases as the processing temperature increases. Moreover, a too low processing temperature (e.g.,280°C), leads to visible surface flow marks on the mouldings and a too high processing temperature (e.g.,340°C) leads to material degradation..

The TG analysis performed with a NETZSCH instrument (type TG 209) proves that PC in 280°C-processed sample has the lowest thermal stability due to mechanical degradation, while the thermal stability modification is insignificant for the samples processed at other temperatures .

The glass transition temperature T_g determination through Differential Scanning Calorimetry (DSC) method using a NETZSCH instrument (type DSC 204) proved that this transition temperature was slightly influenced by the processing temperature, only as a decrease of T_g of processed polymer compared with the granular polymer. This decrease is considered to be the result of an uncomplete material drying prior processing.

It was determined through DMA analyses performed with a NETZSCH instrument (type DMA 242 C) that the stress frequency has an influence both on storage modulus (E') and on loss tangenta (tan δ).

It was calculated the activation energies of the glass transition and it was determined that E_a for this transition is influenced by the processing temperature, as an increase of processing temperature leads to an increase of E_a.

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