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INFLUENCE OF PROCESSING PARAMETERS ON PROPERTIES OF POLYAMIDE FILLED WITH GLASS BALLS

Abstract
Comparative analysis of thermomechanical properties of polyamide and polyamide composites with addition of 30% of glass balls was performed. The specimens were obtained using the injection moulding technology by means of KraussMaffei KM65-160C1 injection moulding machine. The non-filled polyamide and part of components were injected using the parameters recommended by the manufacturer. A reduced value of mould cooling temperature was used for the other non-filled specimens. The differential scanning calorimetry (DSC), hardness testing, impact strength testing, bending resistance and dynamic mechanical thermal analysis (DMTA) were also performed.

Keywords
Polyamide, composites, glass balls, thermomechanical properties

Introduction

Composite materials on polymer matrix have been frequently used in various sectors of the industry. This is caused by the opportunities for improving mechanical properties of the base material and reduction of the price of final products through lower consumption of the polymer [1-3]. Polyamide belongs to the group of nitrogen plastics. Polyamide is a structural material used for manufacturing of e.g. cogwheels, bearings, bolts etc. It is often modified with such additions as glass fibre or graphite. These fillers significantly improve strength properties of the composite [4-6].

Investigations made so far follows that addition of glass beads to the polyamide makes possible to producing a polymer composite with significantly more favorable thermo-mechanical properties compared to unfilled polymer [7]. An essential problem in processing of composites using the injection moulding method is to select adequate process parameters. Insufficiently low value of injection temperature may cause e.g. incomplete filling of the form, depression on the moulded piece surface or improper clamping force. On the opposite, the material with excessive temperature may be degraded. An important point is also the value of mould temperature. The increase in this parameter leads to the increase in the crystallinity degree of semicrystalline materials, which substantially affects mechanical properties of the moulded piece. However, excessively high value of mould temperature may cause degradation of the material [8-10].

The aim of this study was to analyse the effect of processing conditions on thermomechanical properties of polyamide 6 with addition of 30% of glass balls. Schulnamid 6 GB30H was used as a material for the examinations. The differential scanning calorimetry (DSC), hardness testing, impact strength testing, bending resistance and dynamic mechanical thermal analysis (DMTA) were also performed.

Research methodology

Polyamide 6 (with commercial name Schulnamid 6 GB30H manufactured by Campus Plastics) was used in the study. Glass balls with the diameter of 20 μm were used as a filler. The specimens were obtained using the injection moulding technology by means of KraussMaffei KM65-160C1 injection moulding machine.
The specimens made of non-filled polyamide and the polyamide with addition of 30% of glass balls were examined. Injection moulding was performed at variable cooling temperature (see Table 1).

Table 1. Parameters of sample processing

Samples	*Mould Temperature [°C]*	*Injection Temperature [°C]*	*Injection pressure [MPa]*	*Holding pressure [MPa]*	*Holding time [s]*	*Cooling time [s]*
PA	90	280	100	45	20	15
Composite I	40					
Composite II	90					

Source: Author's

Differential scanning calorimetry was performed using NETZSCH PC 200 machine. The specimens were weighted by means of the SARTORIUS scales with precision of 0.01 mg, internal calibration option and closed weighing space. The mass of the specimens ranged from 7 to 12 mg. The DSC curves were recorded during heating of the specimens with the rate of 10 °C/min within the range of temperature from 35 to 250°C. The crystallinity degree and value of temperature of physical transitions was evaluated using NETZSCH software. This software allows for examination of the profile of specimen melting at the given temperature range and determination of the surface area between the thermographic curve and the basic line in the range of endothermic reflex. The degree of crystallinity (Sk) of the filled specimens was calculated based on the following equation [11]:

$$S_k = \frac{\Delta H_m}{w_c \Delta H_k} 100\% \quad (1)$$

where:
ΔH_m – enthalpy of fusion for the material examined,
ΔH_k – enthalpy of fusion for the completely crystalline material (value taken from Netzsch software),
w_c – mass fraction of homopolymer added to the composite examined

Hardness testing was carried out using the ball indentation method. Charpy impact test was employed for evaluation of the impact strength using the pendulum hammer 5 J. Before the test, an A notch was cut out on the specimens. The static bending test was carried out by means of the strength testing machine Inspekt Desk 20 (Hegewald&Peschke). Analysis of dynamic thermal properties was performed using NETZSCH DMA 242 device with a holder for three-point free bending of the specimen in the form of a beam with dimensions of 50x10x4 mm. The specimens in the holder were subjected to sinusoidal force with the frequency of 1Hz and 10Hz with constant amplitude while heating the specimens at the rate of 3°C/min from 25°C to 160°C. The value of the storage modulus E', loss modulus E" and mechanical loss coefficient tgδ were calculated based on the values of forces and strain with regard to the dimensions of the specimens.

Results and discussion of research

Results obtained for differential scanning calorimetry are presented in Table 2 and Figs. 1 and 2.

Table 2. Results of DSC investigations

Samples	*Degree of crystallinity [%]*	*Melting range [°C]*	*Max. Melt temperature [°C]*
PA	26,07	213,6 – 231,2	226
Composite I	26,80	217,5 – 228,1	223,4
Composite II	28,04	215,7 – 226,4	222,6

Source: Author's

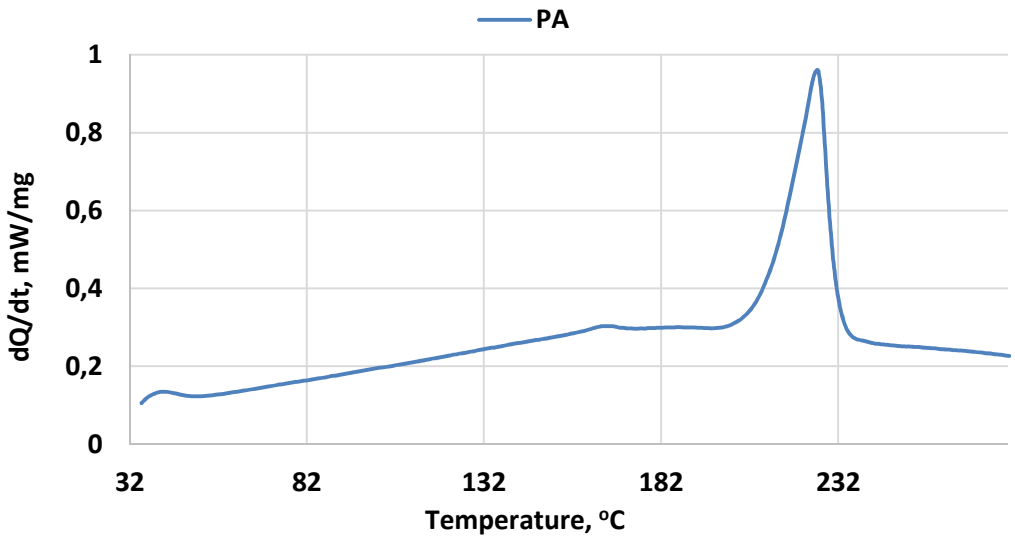

Fig. 1. Thermogram of polyamide.
Source: Author's

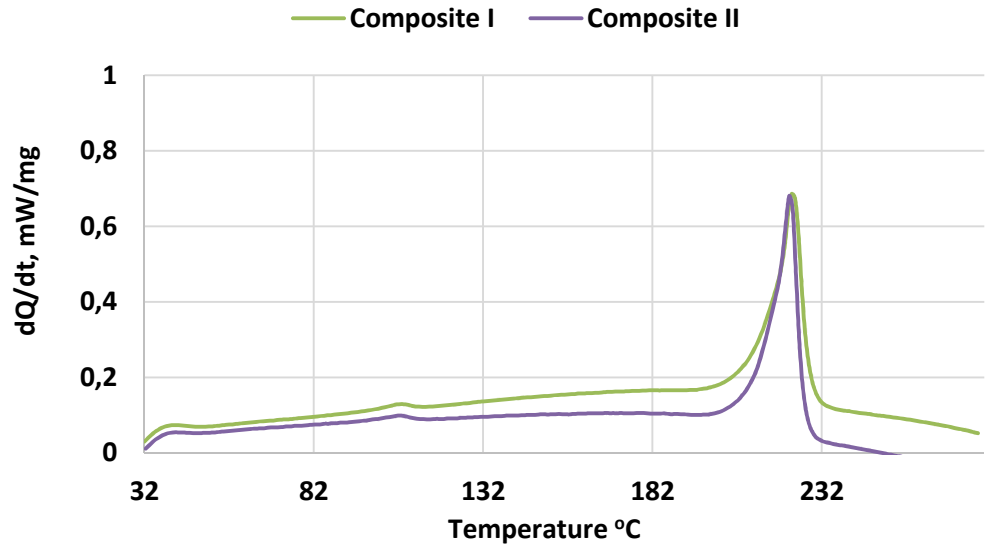

Fig. 2. Thermogram of composites.
Source: Author's

The highest range of melting points was observed for polyamide without filler. The range of melting of the crystalline phase was narrowed for the specimens filled with glass balls. The highest temperature with maximum melting peak was also found for the non-filled material. Addition of the filler caused a decline in the value of this temperature.

For the composites marked as I and II, an increase was observed in the value of the degree of crystallinity compared to the specimens made of non-filled polyamide. This is caused by the effect of filler, which, when cooled down, leads to the formation of the centres of nucleation, which impacts on the increase in the content of the crystalline phase of the polymeric matrix in the composite [12]. The highest value of the degree of crystallinity was observed for the specimen denoted as II, which is caused by the mould temperature higher compared to the specimen I.

The results of the hardness testing are compared in Fig. 3

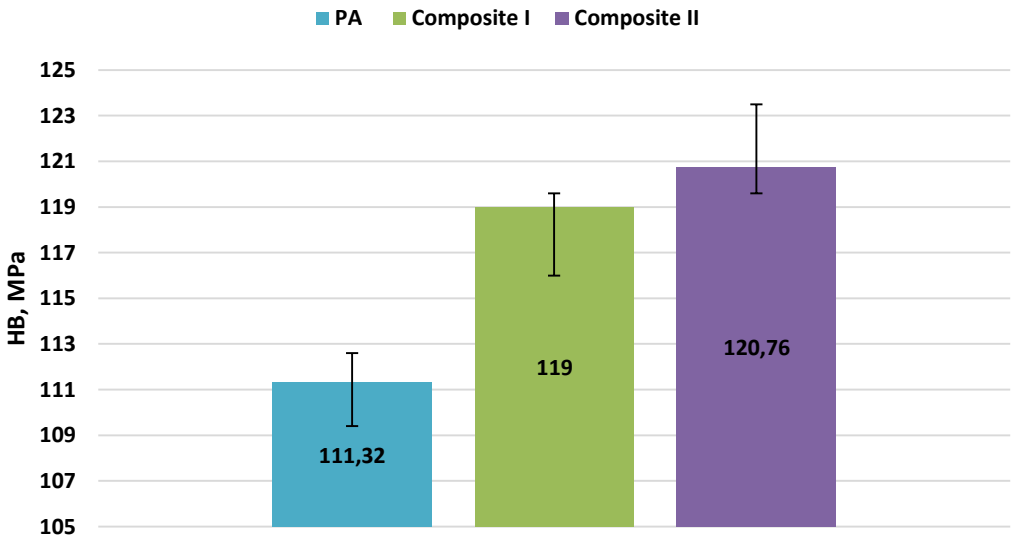

Fig. 3. Results of hardness investigations
Source: Author's

The lowest hardness was observed for the non-filled polyamide. The the presence of glass balls substantially improved hardness of the specimens. The highest hardness was recorded for the composites injected to the mould with temperature of 90°C. Slow cooling rate and the related increase in the degree of crystallinity also impacts on the increase in the hardness of polymeric matrix.

The results of the impact tests are presented in Fig. 4. The highest value was found for the specimens made of non-filled polyamide. It was found that the composite specimens showed a noticeable relationship between impact strength and mould temperature. Lower impact strength was observed with respect to the material without filler for the specimens made in cooler moulds. Reduced impact strength was also found in the specimens injected in the same conditions as polyamide without filler, which represented a decline in the value by 50% compared to the non-filled plastic.

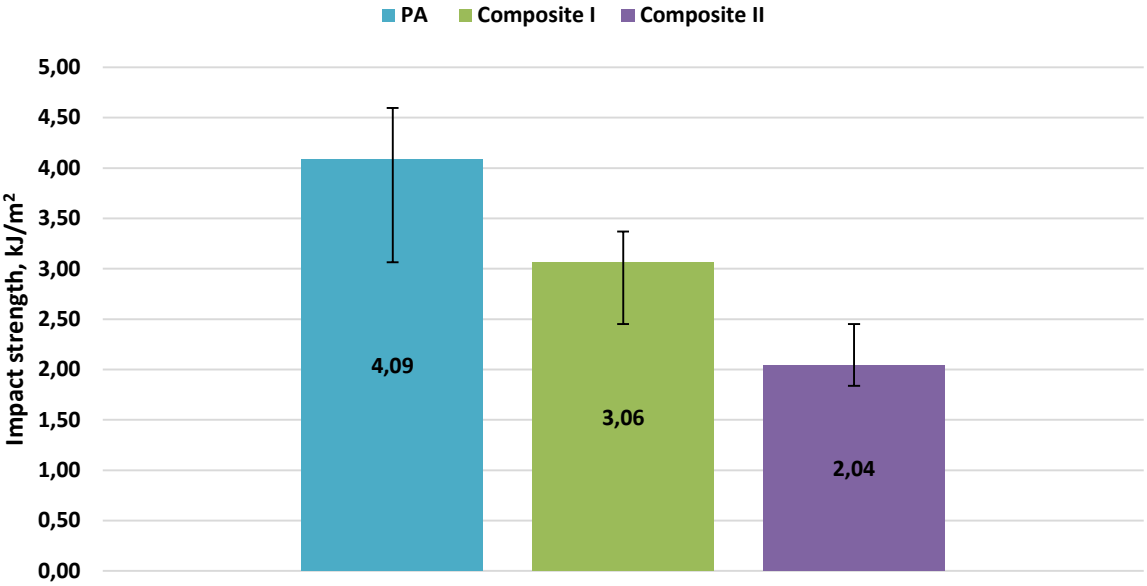

Fig. 4. Results of toughness investigations
Source: Author's

Figs. 5 and 6 illustrate the results of the bending strength measurements. The increase in the bending strength was found for the composites with glass balls. Furthermore, the correlation between this property and mould temperature is insignificant.

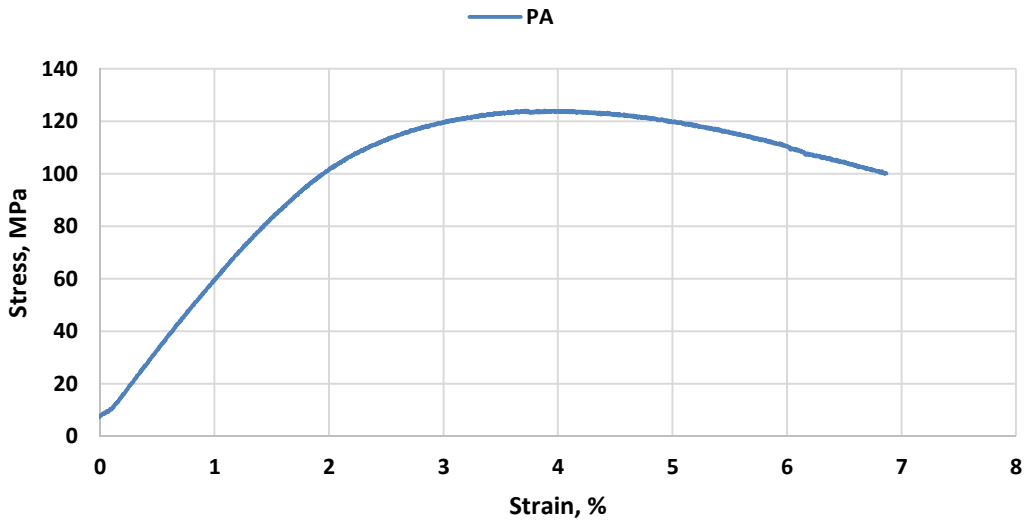

Fig. 5. Results of bending strength investigations of polyamide
Source: Author's

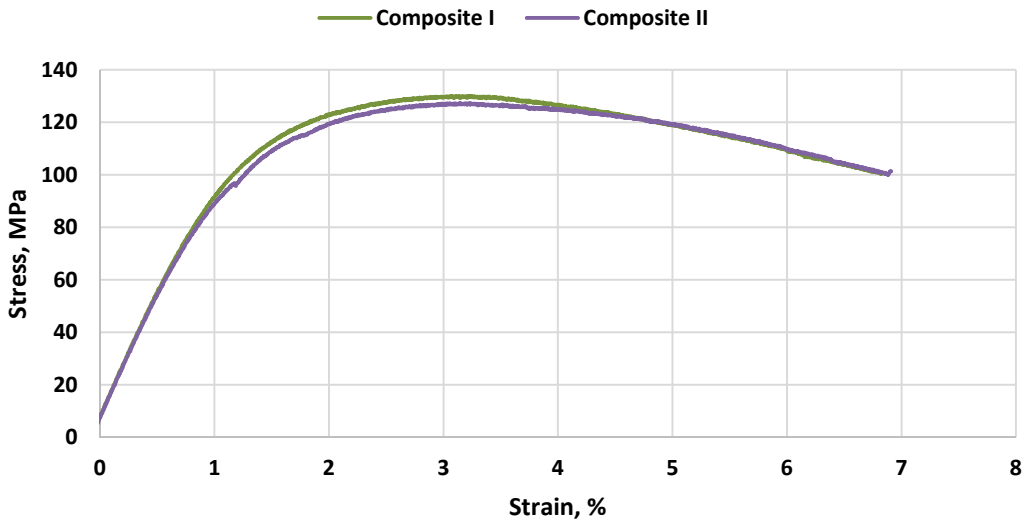

Fig. 6. Results of tensile bending investigations of polyamide of composites
Source: Author's

The results of the dynamic mechanical properties analysis are presented in Figs. 7, 8 and 9. The diagrams illustrate changes in storage modulus and tangent of mechanical loss angle depending on temperature at the frequency of 1 and 10 Hz.

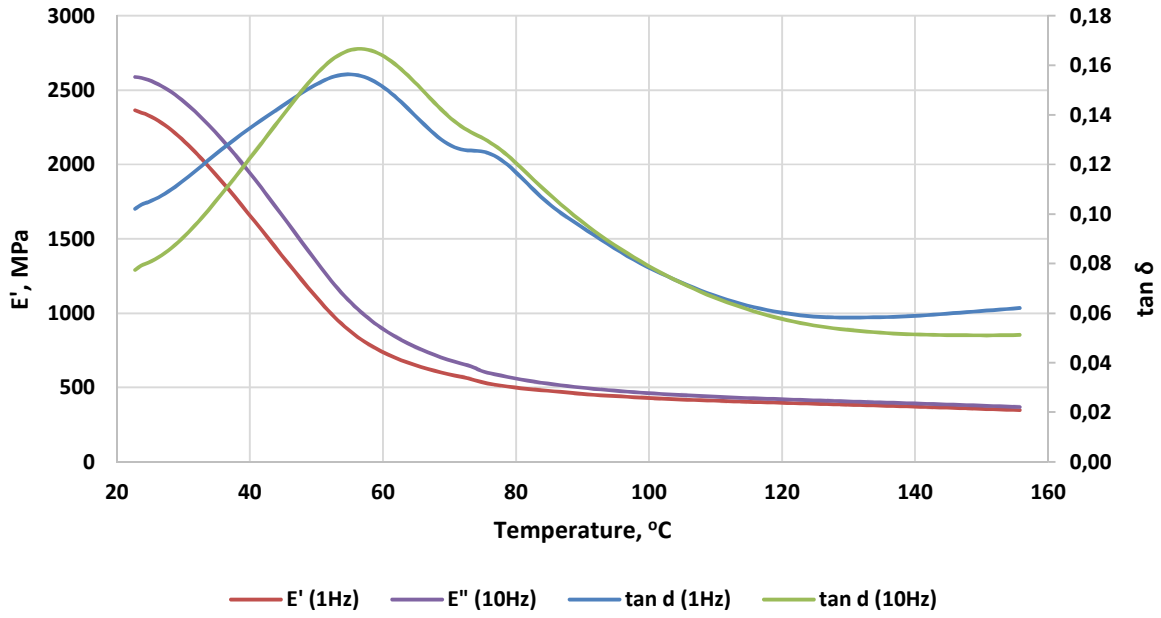

Fig. 7. Results of DMTA investigations of polyamide
Source: Author's

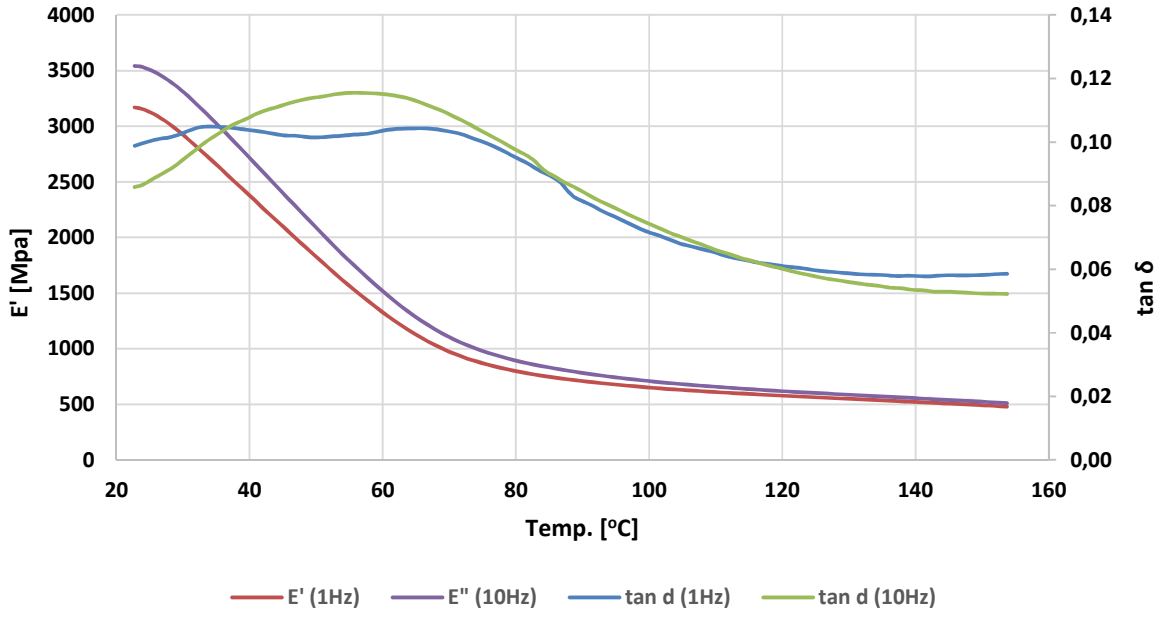

Fig. 8. Results of DMTA investigations of composite I
Source: Author's

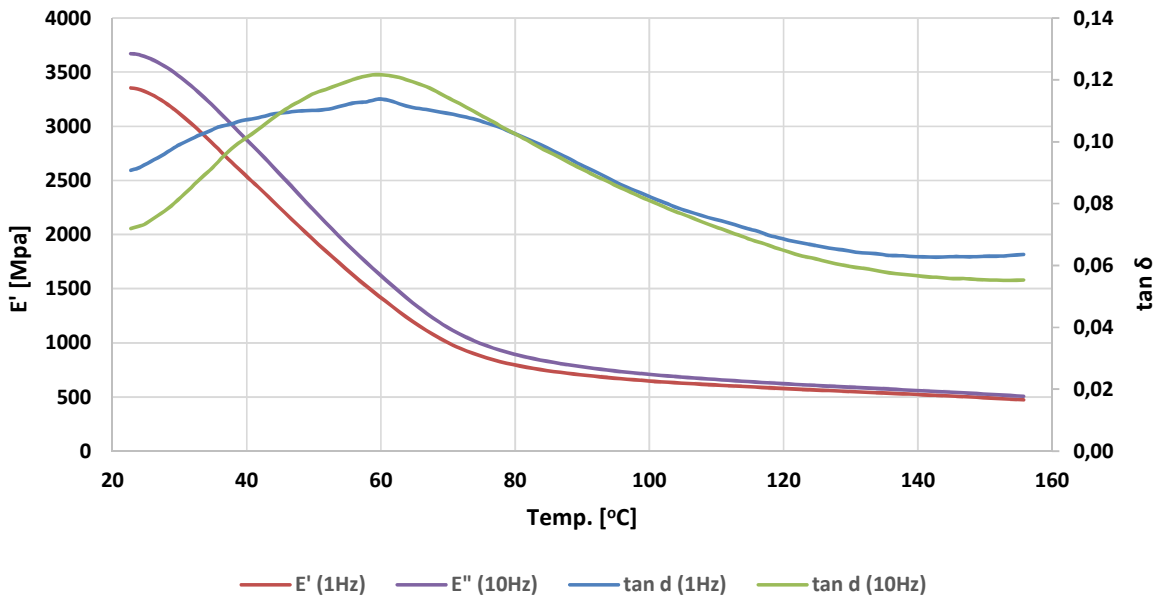

Fig. 9. Results of DMTA investigations of composite II
Source: Author's

The character of curve profiles is the same for all the specimens studied. However, changes concerning the value of storage modulus can be observed. For the specimens containing glass balls, the values of E' are substantially higher than for the non-filled material. This increase is noticeable over the whole temperature range. However, it is the highest in the functional temperature range and reaches ca. 700 MPa. In the phase of high-elastic strain, the difference is not very significant. Changes in the tangent of mechanical loss point to the increase in stiffness of the composite and to vibration damping. The analysis also revealed that the reduction in the mould temperature to the value of 40°C does not cause significant changes in the dynamic properties of the materials studied.

Summary and conclusions

Analysis of the results showed that the reduction in the injection mould temperature from 90 to 40°C does not have a significant effect on the properties of the polyamide composites with glass balls. The composites injected at reduced mould temperature were characterized by lower values of the degree of crystallinity and hardness. However, these differences were insignificant. It was found that lower value of mould temperature has a positive effect on specimen impact strength. No effect of mould temperature on bending strength was observed for the composites analysed. Similarly, no bigger changes in the storage modulus were found during examinations of dynamic mechanical properties. Injection of polyamide composite with glass balls with reduced mould temperature allows for shortening of production cycle time and reduction in energy consumption connected with heating of the mould to higher temperatures, consequently leading to a less harmful effect on the environment.

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