MECHANICS
Vol. 28 No. 4 2009

Andrzej MŁYNIEC*, Tadeusz UHL*

HUMIDITY-TEMPERATURE AGEING AND GLASS FIBER CONTENT INFLUENCE INTO MATERIAL DEGRADATION – PLASTIC SNAPS WITH TORSIONAL BEAMS ANALYSIS

SUMMARY

A study in accelerated humidity-temperature ageing of plastic snaps made of glass-fiber-reinforced composites based on poly(butylene terephthalate) is reported. Samples in the form of latches with torsional beams, manufactured from PBT with various contents of glass fibers (10, 20 and 30%) were subject to accelerated ageing with the use of three various ageing cycles: two kinds of Humidity-Temperature Cycling and simple thermal ageing. The obtained results showed decrease in attenuation during cyclic sample loading process and decrease in weight caused by hydrolysis and a decrease of – 5% to – 35% in ultimate deflection to failure with ageing according to the embrittlement of the matrix and change in adhesion between fiber and matrix.

***Keywords**: polimer ageing, Humidity-Temperature Cycling, glass fibers*

WPŁYW STARZENIOWYCH CYKLI TEMPERATUROWO-WILGOTNOŚCIOWYCH ORAZ DODATKÓW WŁÓKIEN SZKLANYCH NA DEGRADACJĘ MATERIAŁU – ANALIZA ZATRZASKÓW Z BELKĄ OBROTOWĄ WYKONANYCH Z TWORZYW SZTUCZNYCH

W artykule przedstawiono wpływ przyśpieszonego starzenia zrealizowanego za pomocą cykli temperaturowo-wilgotnościowych na zachowanie zatrzasków wykonanych z tworzyw sztucznych na bazie Politeraftalenu-Butylenu wzmacnionego włóknami szklanymi. Próbki w postaci zatrzasków z belką obrotową, wykonane z materiału PBT z różnym dodatkiem włókien szklanych (10, 20 oraz 30%) poddane zostały przyśpieszonemu starzeniu przy użyciu różnych cykli starzeniowych: dwóch cykli temperaturowo – wilgotnościowych oraz czystego starzenia temperaturowego. Uzyskane wyniki wskazują na spadek tłumienia w trakcie obciążeń cyklicznych, spadek wagi próbek spowodowany zjawiskiem hydrolizy oraz zmniejszenie o 5 do 35% maksymalnego ugięcia belki. Zjawisko to związane jest ze zwiększeniem kruchości osnowy polimerowej oraz zmianą adhezji pomiędzy włóknami i osnową wynikającą z degradacji polimeru.

***Słowa kluczowe**: starzenie polimerów, cykle temperaturowo-wilgotnościowe, włókna szklane*

1. INTRODUCTION

Latch elements are currently encountered almost in all products made of plastic materials. They operate under various environmental conditions, which impact substantially the behaviour of their base materials. Mechanic polymer properties are affected significantly by such factors as among the others: temperature, deformation velocity, which is related with viscoelasticity, moreover humidity and percentage water contents in material (Broughton and Maxwell 2007). Under real operating conditions, elements manufactured from plastic materials are often subjected to unfavorable factors degrading their properties, including high temperature (Wright 2001) and high humidity (Mohd Ishak *et al.* 2000). The majority of polymer materials absorb a certain quantity of moist from the surrounding environment, which may cause the swelling, reduction of polymer glass transition temperature (Tg), change of mechanic properties (rigidity, durability, hardness and damping) (Djumaev and Takahashi 1994) as well as degradation and destruction of material surface. While moisture absorption process takes place instantly, diffusion of water through thick cross sections may take even months before the whole material is saturated. Moisture absorption velocity depends on such factors like temperature or mechanical load imposed on the element in question as well as presence of reinforcing additives. Plastic materials reinforced with glass fibers exhibit increased moisture absorption (Boukhoulda 2006) in longitudinal direction relative to fiber direction, in the effect of capillary interaction, which may result in hydrolytic destruction of interaction between fibers and matrix, resulting in the loss of capacity to transfer mechanic load between polymer fibers and matrix. Polymers have their characteristic glass transition temperature, above which they enter into a highly plastic state, where hydrolysis can occur in presence of water. This causes destruction of long polymer chains – chain scission, accompanied by creation of such polymer degradation products as phtalic acid (Mohd Ishak *et al.* 2000). Poly(butylene terephthalate) has glass transition temperature of approximately 70°C, which is clearly indicated by the peak on the diagram of logarithmic attenuation coefficient, resulting from phase transition at this

* Department of Robotics and Mechatronics, Faculty of Mechanical Engineering and Robotics, AGH University of Science and Technology, Krakow; mlyniec@agh.edu.pl

temperature. The impact of sample drying process after ageing tests was also examined. Partial return to initial properties for temperatures below Tg threshold was observed, along with virtually lack of impact for materials aged above glass transition temperature. This indicates that hygrothermal ageing is not an exclusively physical process but rather a physical-chemical process. Interaction with water particles results in irreversible destruction of the material.

M.P. Foulc *et al.* (2005) indicated that glass transition temperature Tg decreases along with polymer ageing, when examining hygrothermal ageing for Glass Reinforced PET material,. This is also accompanied by decrease in Young module value and Poisson number.

Polymer materials subject to cyclic load **scatter energy**, which is observed on the chart in the form of **hysteresis**. Occurrence of hysteresis is related with such phenomena as:

- **Internal friction** resulting from rearrangement of molecular structure as the result of applied load and further sliding between polymer chains. The phenomena of internal friction and internal viscosity significantly depend on temperature. Temperature increase results in increased mobility for polymer particles that causes decrease in viscosity, which further decreases the observed hysteresis. The presence of filling material results in decrease in particle mobility, which in turns increases viscosity and hysteresis.
- **Distortion induced crystallization** consists in melting and creation of crystal structures during periods of substantial extending distortion and subsequent compression.
- **Modification and rearrangement of polymer particles** during several beginning distortion cycles results in decrease of rigidity and changes in attenuation characteristics – Mullin's effect.

Positive impact of glass fibers on load carrying capacity of materials has been proven already numerous times (Mohd Ishak *et al.* 2000; Pegoretti *et al.* 2006; Bergeret *et al.* 2001; Ward and Sweeney 2005; Abdulkadir Gullu *et al.* 2006). In the result of increase in quantity of embedded glass fibers, load carried by polymer matrix decreases along with the increase in stress levels necessary to initiate destructive processes. At the same time, maximum distortion is also decreased.

Plastic materials reinforced with glass fibers, subjected to temperature ageing as the result of difference in thermal expansion coefficients of fibers and matrix, may also cause induction of internal stress reducing effectiveness of bonding between fibers and matrix (Broughton and Maxwell 2007). This may result in thermo-mechanical material degradation. Sudden temperature changes may result in thermal spiking, resulting in creation of substantial local stress, impacting mechanical structure properties in a negative manner.

2. EXPERIMENTAL

During the aforementioned research covering material ageing processes, sample latches with rotating beams were used, manufactured from polybutylene terephthalate (PBT) with 10, 20 and 30% content of glass fibers, PBT GF10, PBT GF20 XF (easy flow) and PBT GF30.

Tests were carried out under laboratory conditions at temperature of 23^{o}C, with relative air humidity 50%, using Zwick Z0.5 strength testing machine. Sample latches and cylindrical rod (5.5 mm diameter) were used to provide displacement along the Z axis (Fig. 1).

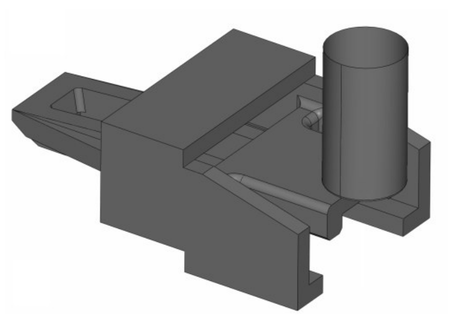

Fig. 1. The shape of examined samples with cylindrical element providing displacement

Tests were performed with displacement velocity 0.8 mm/min, 50 mm/min and 800 mm/min. Hysteresis was obtained for displacement 1.4 mm. Sample weight was measured with 1 mg precision.

Samples were subjected to accelerated ageing with the use of three various ageing cycles:

- **Humidity-Temperature Cycling 1** (H-T 1) – with temperature of 95^{o}C set under conditions of increased (controlled) humidity (95%) (Fig. 2). 40 cycles, each 8 hours' long, were programmed.

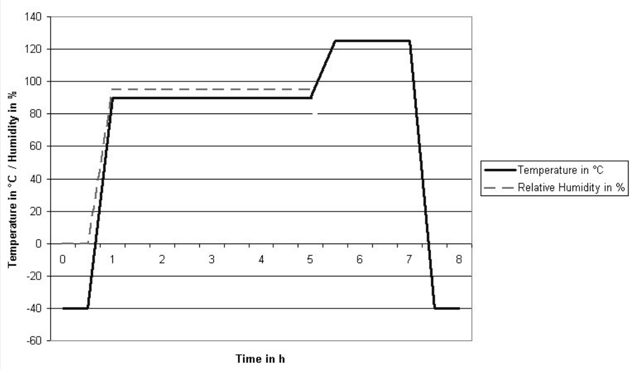

Fig. 2. The shape of Humidity-Temperature Cycling 1

- **Humidity-Temperature Cycling 2** (H-T 2) – with temperature of 55^{o}C set under conditions of increased (controlled) humidity (99%) (Fig. 3). 5 cycles, each 24 hours' long, were programmed. Each cycle was compliant with ISO 8092 standard.

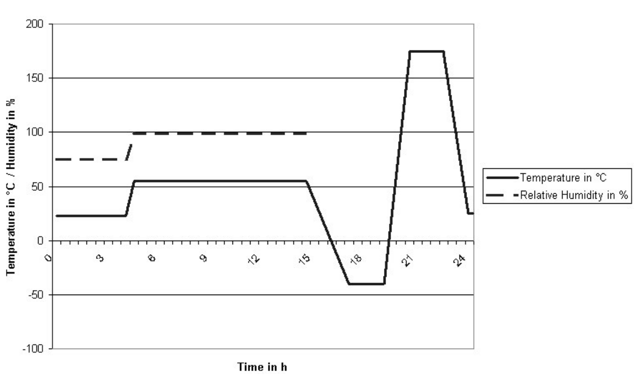

Fig. 3. The Shape of Humidity-Temperature Cycling 2

– **Temperature ageing 288 h under temperature of 175°C** with external air replacement, 40% per hour.

3. RESULTS AND DISCUSSION

Impact of ageing process on sample weight

During tests, decrease in sample weight subject to Humidity-Temperature Cycling was observed. The largest mass loss was observed for PBT GF20 samples. It must be taken into account that PBT GF20 as a material has improved flow properties. It is possible therefore to conclude that application of plasticizers, facilitating filling target moulds, results in increased mass loss for samples subject to ageing process. A hydrofilization phenomenon also substantially affects mass loss, introducing certain error to the concluded tests. Samples exposed to pure ageing process exhibit larger mass loss than samples subjected to Humidity-Temperature cycles. Decreased mass loss during H-T cycles is related with the quantity of water absorbed during ageing cycles and creation of hydrolysis by-products (Tab. 1). The obtained results are consistent with research conducted by Foulc *et al.* (2005), who observed substantial changes in molecular weight during hygrothermal ageing process, along with creation of such hydrolysis by-products as phtalic acid and its derivatives.

Impact of ageing process and fiber quantity on stabilization of force-displacement chart. Mullin's effect

Research results indicate that increase in fiber quantity impacts not only the size of hysteresis (and appropriately affecting also attenuation) but also behavior of examined element subject to repeated load. Figures 4–6 present behavior of the examined element subject to 3 distortion cycles (indicated by the visible hysteresis) and then destructive distortion. Along with the increase in fiber contents in material, this chart is shifted further right, increasing distortion after each subsequent force input.

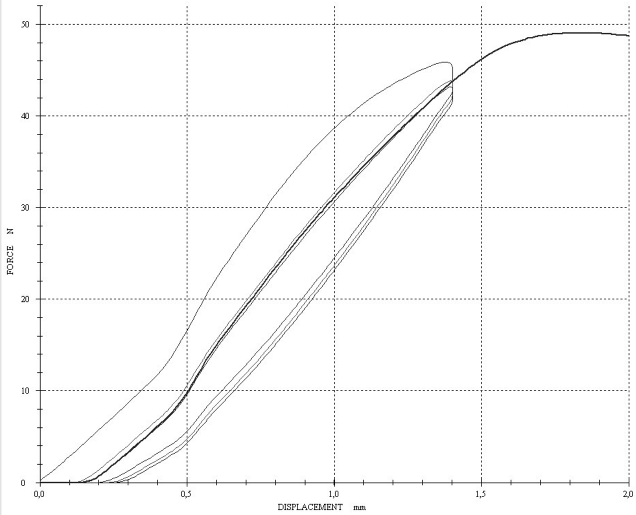

Fig. 4. Cyclic distortion and destruction of PBT GF10 sample after H-T 2 ageing cycle

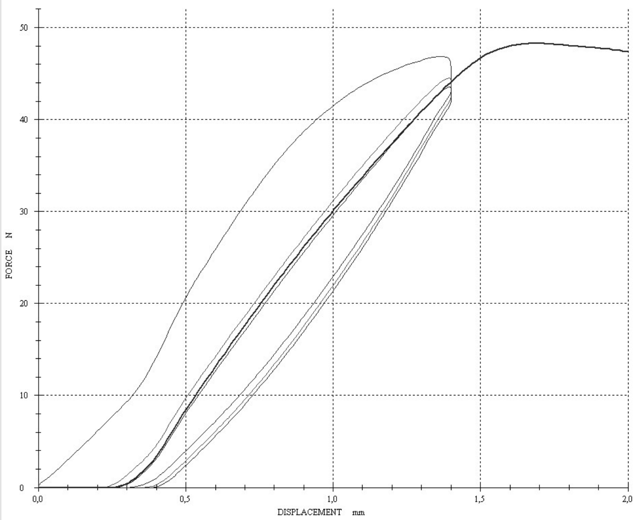

Fig. 5. Cyclic distortion and destruction of PBT GF20 sample after H-T 2 ageing cycle

Table 1

Percentage weight change during ageing cycles related to AR (As Received) samples

Ageing Profile	H-T 1			Temp.	H-T 2	
Ageing time	**80 h**	**180 h**	**320 h**	**288 h**	**65 h**	**120 h**
PBT GF10	0.02	0.04	0.06	0.27	0.06	0.09
PBT GF20	0.43	0.5	0.58	1.45	0.74	0.58
PBT GF30	0.05	0.06	0.21	0.39	0.21	0.28

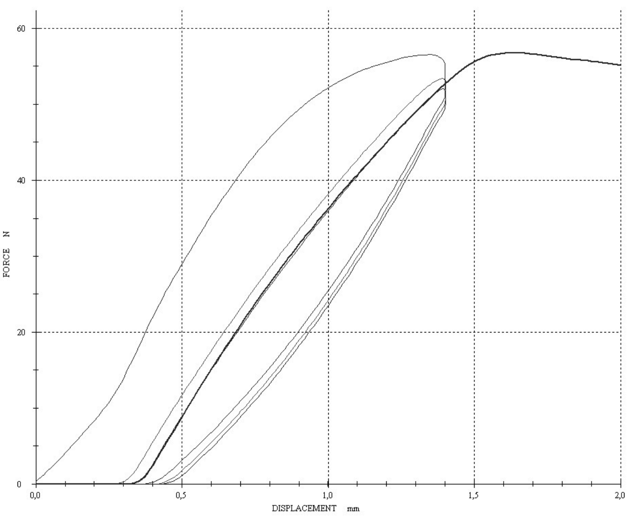

Fig. 6. Cyclic distortion and destruction of PBT GF30 sample after H-T 2 ageing cycle

Table 2

Observed chart shift after first sample load

Shift after first load	AR state	H-T 1	Temp.	H-T 2
PBT GF10	0.13	0.1	0.09	0.13
PBT GF20	0.22	0.15	0.15	0.23
PBT GF30	0.31	0.18	0.2	0.26

Table 2 contains the collection of data regarding distortion observed for the examined sample after the first load cycle. The said distortion decreases along with material degradation, which can be clearly observed from the presented data. This can be related directly to deterioration of viscoelastic properties of examined material. Based on this observation, it can be concluded that ageing according to H-T 1 profile is comparable to ageing under temperature of 175°C.

Impact of ageing profile on maximum snap deflection

Application of a larger number of glass fibers results in limitation of material degradation, which is related with the fact that polymer matrix carries smaller mechanical load. The obtained results are consistent with the research results for PBT-glass fiber and PBT-CSR-glass fiber materials conducted by M. Ishak (2000). The larger degradation was observed for PBT GF10 material, which decreased destructive distortion by more than 30% (Fig. 7). The remaining samples, subjected previously to cyclic mechanic load, exhibited smaller deterioration in their properties when compared with samples distorted for the first time (Fig. 8).

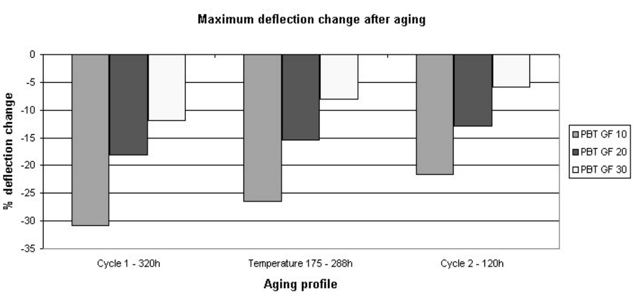

Fig. 7. Maximum deflection change after H-T Cycling 1, Temperature ageing and H-T Cycling 2 (first usage)

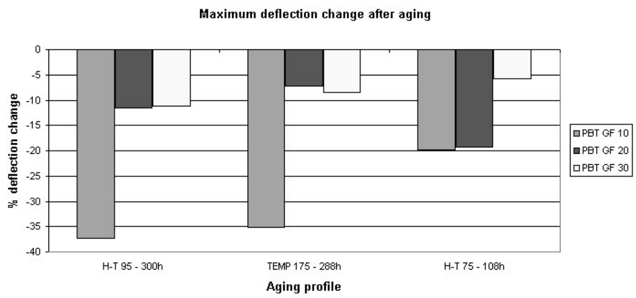

Fig. 8. Maximum deflection change after H-T Cycling 1, Temperature ageing and H-T Cycling 2 (test after 3 hysteresis test)

Impact of testing velocity on force – displacement chart

Distortion velocity has key importance for plastic materials. Along with the increase in the said velocity, attenuation increases, thus increasing the force level required to destroy the examined sample (Fig. 9) and decreasing maximum distortion, which is consistent with research results obtained by M. Ishak *et a*l. (2000). This particular phenomenon is related closely with the increase in PBT matrix embrittlement, subject to rapid distortion variations, resulting from viscoelasticity properties of polymer materials. During high velocity distortions, such phenomena as segmental mobility and plastic deformation process play increasing role in creation polymer crazing.

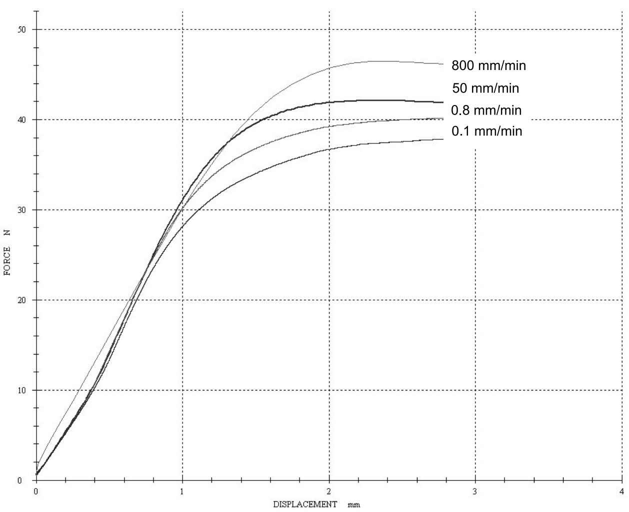

Fig. 9. The impact of testing velocity on force – distortion chart for a sample under AR (As Received) condition

Impact of ageing profile on cracking mechanism

Poly butylene terephthalate with 10% contents of glass fibers under AR condition is considered a tough material. The presence of glass fibers increases toughness in the result of occurrence of such mechanisms as fiber pull-out and debonding (Ishak *et al*. 2000). In the result of ageing processes, polymer matrix is subject to hydrolysis and bonding between fibers and matrix are weakened, which means that the examined material loses its load carrying capacity. The conducted tests confirmed changes in the observed cracking mechanism from ductile to brittle for H-T 1 profile and temperature ageing. Fiber-pull out destruction mechanism remains dominant though it is also possible to observe (Ishak *et al*. 2000; Broughton and Maxwell 2007) lack of strict adherence between PBT matrix and fibers as well as occurrence of material crazing.

Impact of ageing profile on hysteresis

In the result of material ageing process, decrease in hysteresis under cyclic load conditions can be observed. Decrease in hysteresis, i.e. decrease in energy dissipation, can be related with changes in internal friction, viscosity and mobility of polymer chains. The conducted tests indicate that the largest decrease in hysteresis size was caused by Humidity-Temperature Cycling 1 (H-T 1) and temperature ageing (Temp). In both cases, decrease in energy dissipation was observed. However, after H-T 2 ageing cycle, minor increase in attenuation was observed, visible on charts in the form of increased hysteresis. These phenomena are related to various phases of material degradation. Polymers subject to water undergo plasticization, resulting in decrease in glass transition temperature, while increasing polymer chain mobility, which can be observed in the form of increased hysteresis. In the following material degradation phase, under the influence of water and high temperature (above glass transition temperature Tg), material is subjected to irreversible chemical degradation: hydrolysis. Hydrolysis can have two different mechanisms: random polymer chain cutting or classic polymer degradation (Ishak *et al*. 1998). As the result of such substantial structural changes, molecular mass of the examined plastic material decreases, along with the decrease in polymer segment mobility. This process can be observed on the charts in the form of decreased hysteresis. During the conducted test, it was also observed that in the result of material degradation, the slope angle for force – displacement curve is also altered (Fig. 10). This is directly related with decrease in attenuation, resulting in decrease of force magnitude required to distort the examined sample by some predefined value.

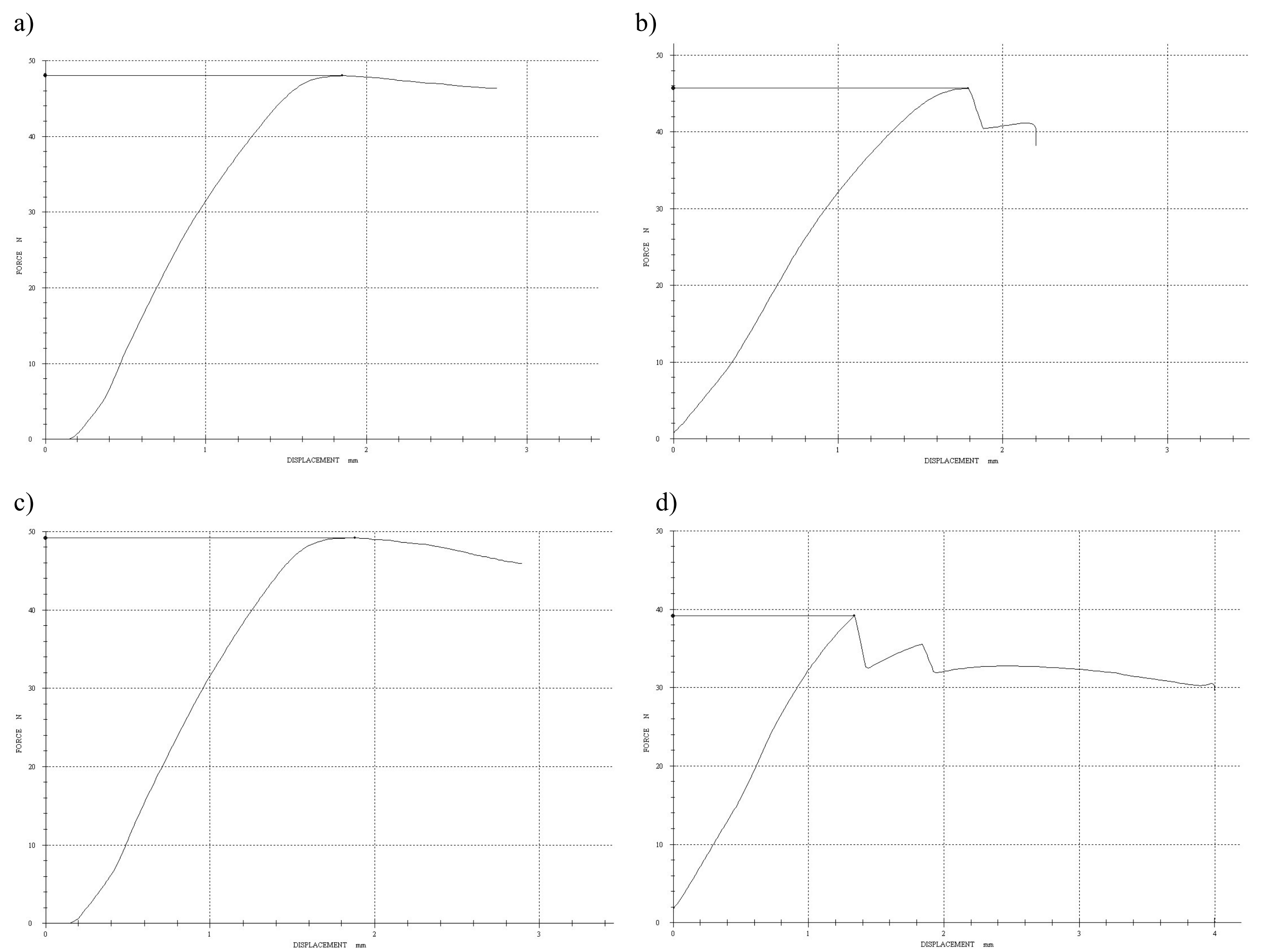

Fig. 10. Impact of ageing profile on fracture mechanism for PBT GF10 material: a) sample AR; b) profile H-T 1; c) profile H-T 2; d) temperature profile

Table 3

The impact of ageing profile on quantity of dissipated energy and changes in slope angle for force – distortion chart relative to AR samples

Glass fiber content	10% Glass Fibers				20% Glass Fibers				30% Glass Fibers			
Specimen	**AR**	**H-T 1**	**H-T 2**	**Temp.**	**AR**	**H-T 1**	**H-T 2**	**Temp.**	**AR**	**H-T 1**	**H-T 2**	**Temp.**
Energy dissipated [Nmm]	12.460	10.410	11.192	9.899	17.917	11.933	18.955	12.676	26.941	18.224	26.338	18.295
Decrease of hysteresis [%]	n/a	–16.453	–10.176	–20.553	n/a	–33.398	5.793	–29.252	n/a	–32.356	–2.239	–32.092
Change in slope angle for force – displacement chart [%]	n/a	–18.392	0.284	–10.879	n/a	–14.542	8.720	–15.374	n/a	–12.956	–4.477	–20.5932

Table 3 indicates that the largest decrease was observed for samples subjected to temperature ageing and H-T 1 ageing cycles, just like in the case of decrease in hysteresis. It is also possible to observe that for samples subjected to H-T 1, decrease in chart slope angle decreases along with the increase in glass fiber contents in the base material.

4. SUMMARY AND CONCLUSION

One of the most important aspects in the product development, which must be taken into consideration, is the prediction of the product lifetime. Fiber-reinforced polymer composites are widely used in aerospace and automotive applications where changes in physical and mechanical properties of composite components can influence their functionality. The absorbed water, above a threshold defined for a given temperature and a given ageing time, results in more undesirable effects on the mechanical properties of these materials since the not only interacts with polymer matrices, physically, i.e. plasticization, and/or chemically, i.e. hydrolysis of the ester groups, as in the unfilled systems but also attacks the fiber-matrix interface, which results in embrittlement of the fiber-reinforced PBT composite.

Such factors may cause material degradation, which in turns means that the material will lose its load carrying capacity. Based on the completed tests, it is possible to conclude that the largest decrease in material properties is caused by cooperation between high moisture and temperature exceeding glass transition temperature for the examined plastic material. Under such unfavorable conditions, attenuation decreases which can be observed in the form of decrease in hysteresis size and decrease in the magnitude of force necessary to destroy the examined sample. At the same time, material fracture mechanism changes from ductile to brittle. The above-presented results can be used in further, more elaborate research on ageing polymer materials.

Acknowledgments

Author would like to acknowledge the support of the Delphi Technical Center Krakow. Thanks are due also to the E/EA DCS Team for sample providing and all their technical assistance.

References

Mohd Ishak Z.A. *et al*. 2000, *Hygrothermal ageing and fracture behavior of short-glass-fiber-reinforced rubber-toughened poly(butylene terephthalate) composites*. Composites Science and Technology 60 (2000) 803–815, Elsevier London.

Pegoretti A. *et al.* 2006, *Strain recovery of post-yied compressed semicristalline poly (butylene terephthalate)*. Polymer 47 (2006) 5862–5870, Elsevier London.

Bergeret A. *et al.* 2001, *The hygrothermal behavior of glass-fiber-reinforced thermoplastic composites: a prediction of the composite lifetime.* Polymer Testing 20 (2001) 753–763, Elsevier London.

Ward I.M., Sweeney J. 2005. *An introduction to the mechanical properties of solid polymers*. Willey.

Abdulkadir Gullu *et al*. 2006, *Experimental investigation of the effect of glass fibers on the mechanical properties of polyprolylen and polyamide 6 plastics*. Materials and design 27 (2006) 316–323, Elsevier London.

Boukhoulda B.F. 2006, *The effect of fiber orientation angle in composite material on moisture absorption and material degradation after hygrothermal ageing.* Composites Structures 74 (2006) 406–418, Elsevier London.

Foulc M.P., Bergeret A. *et al.* 2005, *Study of hygrothermal ageing of glass fiber reinforced PET composites.* Polymer Degradation and Stability 89 (2005) 461–470, Elsevier London.

Song M.S., Hu G.X. & Hu L.J. 1998, *Prediction of long-term mechanical behavior and lifetime of polymeric materials.* Polymer Testing 17 (1998) 311–332, Elsevier London.

A.Djumaev A., Takahashi K. 1994, *Effects of moisture absorption on damping performance and dynamic stiffness of NY-6/CF commingled yarn composite*. Journal of Material Science 29 (1994), 4736–4741.

Wright D.C. 2001, *Failure of Plastics and Rubber Products – Causes, Effects and Case Studies involving Degradation.* RAPRA Technology Report, ISBN: 1-85857-261-8.

Broughton W.R., Maxwell A.S. 2007, *Accelerated Environmental Ageing of Polymeric Materials*. Industry and Innovation Division, National Physical Laboratory, Teddington.

Mohd Ishak ZA *et al.* 1998, *Hydrolitic stability of short glass fiber reinforced poly (butylene terephthalate)*. International Conference on Advanced Materials and Processing, Kuala-Lumpur, August.