Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 19
ISSUE 2
December
2006

The influence of annealing on dynamical mechanical properties of polyamide 6 / fiber glass composites

J. Koszkul*, D. Kwiatkowski
Institute of Polymer Processing and Production Management,
Czestochowa University of Technology
Al. Armii Krajowej 19c, 42-200 Czestochowa
* Corresponding author: E-mail address: koszkul@kpts.pcz.czest.pl

Received in revised form 15.07.2006; accepted in final form 30.10.2006

Materials

ABSTRACT

Purpose: of this paper is analysis the the influence of annealing on dynamical mechanical properties of composites PA6 with fiberglass.
Design/methodology/approach: Polamide 6 thermoplastic polymer of trade name Tarnamid T-27 produced by Zakłady Azotowe S.A. in Tarnów (Poland) was used for examinations. E glass fibre, made of non-alkaline boron – aluminium – silicon glass of alkaline oxides content less than 1%, was used for polyamide 6 reinforcement. Polyamide and its composites filled with 10, 30 and 50% of glass fibre were tested. Dynamical mechanical properties of composite matrix were testes for comparative reasons. In order to examine the influence of annealing on mechanical dynamical properties a part of samples were annealed in the air at temperature 170°C. In the test the annealing rate was 0.015°C/s, time 900s per 1mm thickness and the cooling rate 0.01°C/s. Before examinations test specimens were conditioned at 23±20C temperature and 50±5% relative humidity, during 16 h. Test specimens were bent at the frequency 1 Hz and 10 Hz, in the range of temperature from – 100°C to 200°C, at a heating rate 5 deg/min. Deformation amplitude was 16µm. Dynamical properties of polyamide and glass fibre filled composites were examined by the DMTA general – purpose apertures for dynamical tests (Polymer Laboratories).
Findings: DMTA method was used to determine the influence of a fiberglass content on dynamical properties of polyamide composites. The effect of annealing on the plastic properties was also described.
Research limitations/implications: DMTA method was used to determine the influence of a talc content on dynamical properties of polyamide 6 composites in the future.
Practical implications: The results of experiments will allow to determine the recommendations referring to the optimization of processing conditions, and as a result of this polymer will have high mechanical properties
Originality/value: Measurements of dynamical properties are a general – purpose method of examinations of material behaviour under dynamical sinusoidal load.
Keywords: Engineering polymers; Properties; Mechanical properties; DMTA methods

1. Introduction

Many composites having a polymer matrix are obtained by physical modification. The aim of polymer physical modification is receiving its determined properties, mainly physical ones, by filler adding to the plastic state polymer. Obtaining required properties of the composite depends not only on the type of a used filler but also its content, shape and adhesion on the boundary of the polymer and filler [2,4,6-8].

The change of some physicomechanical properties can also be obtained by heat treatment. Most often used heat treatment process is annealing which is carried out in liquid or gas medium.

It is recommended that reaching the annealing temperature should be slow from 0.008 ^{0}C/s to 0.033 ^{0}C/s. The annealing time depends on the thickness of the annealed element and should be 900 s per 1 mm of specimen thickness. The cooling rate should also be small ranging from 0.008 ^{0}C/s to 0.033 ^{0}C/s. It was stated that the biggest changes in the plastic during occurred annealing in the maximum second recrystallization temperature (for polyamide – about 170 ^{0}C). Annealing causes the increase of crystalline phase fracture by about 20% and at the same time decrease of amorphous phase fraction and also the increase of spherulite dimensions. The discussed changes have the significant influence on physicomechanical properties of the plastic [2,3].

Determing the influence of the fibre glass content on dynamical mechanical properties of the polyamide 6 composites was the aim of the presented paper. The effect of annealing on the plastic properties was also described.

Polyamide 6 composites with the fibre glass show the viscoelastic field characteristic. Deformation for such materials depends not only on stress but on load time as well. Viscoelastic properties of these polymers appear in, among other things, that when the specimen undergoes the sinusoidal vibration, changing in time, the arising stress σ shows the phase displacement ε of $0^0 < \delta < 90^0$ in compare to the deformation. We can assume that the deformation is changing according to the following dependence :

$$\varepsilon = \varepsilon_0 \cdot \sin(\omega \cdot t) \qquad (1)$$

where :

ε_0 - deformation amplitude,

ω - angular frequency.

Thus the stress will be :

$$\sigma = \sigma_0 \cdot \sin(\omega \cdot t + \delta) \qquad (2)$$

where :

δ - phase displacement angle.

The lengths of the vibration period is equivalent to the time of stress action in statistical tests. Stress consist of two stress components described by the formulas [4]:

$$\sigma = \sigma_0 \cdot \sin(\omega \cdot t) \cdot \cos\delta + \sigma_0 \cdot \cos(\omega \cdot t) \cdot \sin\delta = E' \cdot \varepsilon_0 \cdot \sin(\omega \cdot t) + E'' \cdot \varepsilon_0 \cdot \sin(\omega \cdot t + 90) \qquad (3)$$

- $E' \cdot \varepsilon_0 \cdot \sin(\omega \cdot t)$ in the phase with deformation,
- $E'' \cdot \varepsilon_0 \cdot \sin(\omega \cdot t + \delta)$ phase displaced.

Young modulus E determined by the method of specimen loading with sinusoidal variable vibration is complex modulus E^*.

$$E^* = E' + E'' \qquad (4)$$

It consist of two components : real E' (conservative modulus), occurring according to the deformation phase and imaginary one E'' (loss modulus), displaced of some angle. Instead of loss modulus E'' the tangent of mechanical loss angle δ is often given

$$\mathrm{tg}\,\delta = \frac{E''}{E'} \qquad (5)$$

In case of Hooke's ideal elastic materials E''=0, and of Newton's ideal viscous materials E'=0. In general for plastic E''<E' [11,14,15,16,17].

DMTA method was used to determine the influence of a glass fibre content on dynamical properties of polyamide composites. Using this equipment, dynamical properties of polyamide composites in relation to the temperature and frequency were determined.

2. Materials, apparatus and methods of tests

Polamide 6 thermoplastic polymer of trade name Tarnamid T-27 produced by Zakłady Azotowe S.A. in Tarnów (Poland) was used for examinations. E glass fibre, made of non-alkaline boron – aluminium – silicon glass of alkaline oxides content less than 1%, was used for polyamide 6 reinforcement.

Polyamide and its composites filled with 10, 30 and 50% of glass fibre were tested.

Dynamical mechanical properties of composite matrix were testes for comparative reasons. In order to examine the influence of annealing on mechanical dynamical properties a part of samples were annealed in the air at temperature 170^{0}C. In the test the annealing rate was 0.015 ^{0}C/s, time 900s per 1mm thickness and the cooling rate 0.01 ^{0}C/s.

Before examinations test specimens were conditioned at 23±2^{0}C temperature and 50±5% relative humidity, during 16 h

Cubicoid test specimens of dimensions according to [5] were tested.

$$\frac{h}{l} \le 0.1 \qquad \frac{b}{l} \le 0.02 \qquad (6)$$

Test specimens were bent at the frequency 1 Hz and 10 Hz, in the range of temperature from – 100^{0}C to 200^{0}C, at a heating rate 5 deg/min. Deformation amplitude was 16µm.

Dynamical properties of polyamide and glass fibre filled composites were examined by the DMTA general – purpose apertures for dynamical tests (Polymer Laboratories).

3. Investigation results and discussion

The relationship between the real modulus E' and the temperature and filler content, at the frequency 1 and 10 Hz, is shown in Fig. 1. The change of real modulus value runs for the frequency of 10 Hz is represented by the blue line and for 1 Hz by the green line.

In Fig. 1. the change of a real number E' in relation to the frequency is also shown. Measurements made at 1 Hz frequency proved that E'(T) relationships are similar to the results noticed at 10 Hz frequency. Values of E'(T) are only a little lower.

In the range of elastic deformation (Fig. 1, range A), for all polyamide 6 composites, there is no influence of the temperature on the modulus. In this range the value of E' modulus is $10^{9.4}\div10^{9.6}$ N/m^2. The annealed polyamide composites show the value of conservative modulus ranging from $10^{9.51}$ to $10^{9.65}$. Glass transition (Fig. 1, range B) is the most evident for polyamide 6. For this material the biggest decrease of the real number E' in relation to the temperature was observed.

In this range the least decrease of the real number was for the composite of maximum glass fibre content. The annealed

polyamide 6 fibre glass composites are temperature less sensitive in the range of glass transition. It is especially visible for the composite with 50% fibre glass content (Fig. 2).

Polyamide 6 after the heat treatment shows the increase in E' value of about 10%. For polyamide 6 composites the glass transition range is much more evident, especially at 50% glass fibre content.

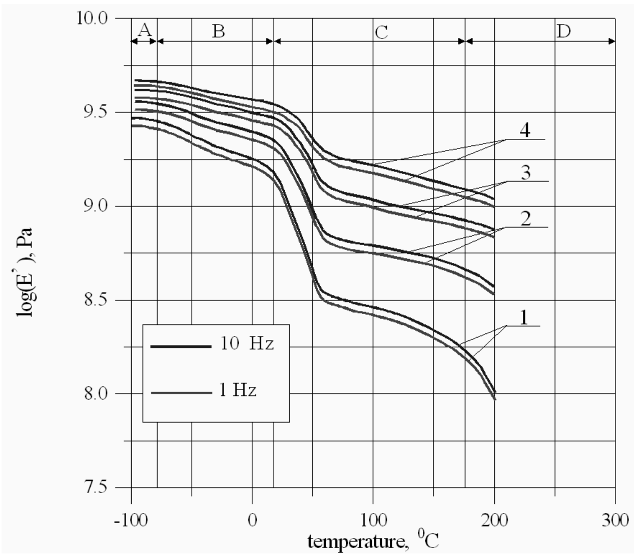

Fig. 1. Values of a real number E' in relation to the temperature T, frequency and glass fibre filler content : 1 – polyamide 6, 2 – polyamide 6 + 10%, 3 – polyamide 6 + 30%, 4 – polyamide 6 + 50%. A – elastic deformation range, B – glass transition range, C – viscoelastic deformation range, D – plastic transition range.

Polymer ability for such deformation mainly depends on a glass fibre content and the higher glass fibre content the lower ability for deformation. In this range values of E' modulus for polyamide 6 decreased of about 1600 MPa and for 50% glass fibre filled polyamide decreased of only about 800 MPa.

The influence of the heat treatment annealing appears with the increasing E' values. The value of the conservative modulus for polyamide 6 in the discussed range of deformations decreases by 1400 MPa and for composite with 50% fibre glass content decrease by 600 MPa.

Similar relationships in the range of plastic transition (Fig.1, range D) are for all tested composites. The biggest decrease of the real number in relation to the temperature was noticed for polyamide 6 and the least one for 50% glass fibre filled polyamide.

Fig. 3 shows the relationship between the loss tangent and the temperature. Glass fibre adding causes gradual decrease of tgδ(T) values for polyamide composites.

It can be stated that the higher filler content the lower tgδ value and the similar dependence is for maximum values. Authors of papers [1,2,6,8,9,10] stated that the degree of crystallinity of polymer have an essential effect on maximum values of tgδ(T) curve and the bigger degree of crystallinity the higher maximum of tgδ(t) curve.

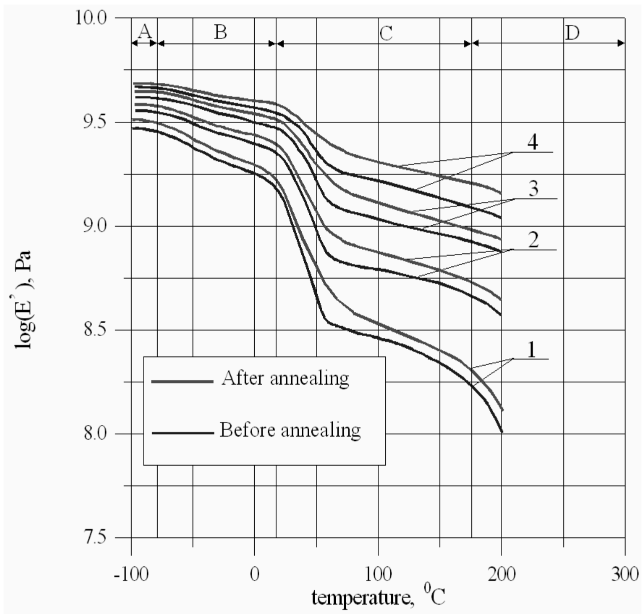

Fig. 2. Values of a real number E' in relation to the temperature T and glass fibre filler content : 1 – polyamide 6, 2 – polyamide 6 + 10%, 3 – polyamide 6 + 30%, 4 – polyamide 6 + 50%. A – elastic deformation range, B – glass transition range, C – viscoelastic deformation range, D – plastic transition range.

When the degree of crystallinity decreases the loss tangent change is similar to the one for amorphous polymer.

Annealing of polyamide 6 and its composites with fibre glass causes the change of crystallite dimensions as well as the modification of their internal structure including the increase in the crystalline phase fraction. Polyamide 6 and its composites with fibre glass after annealing are characterised with higher values of tgδ(T) (Fig.4).

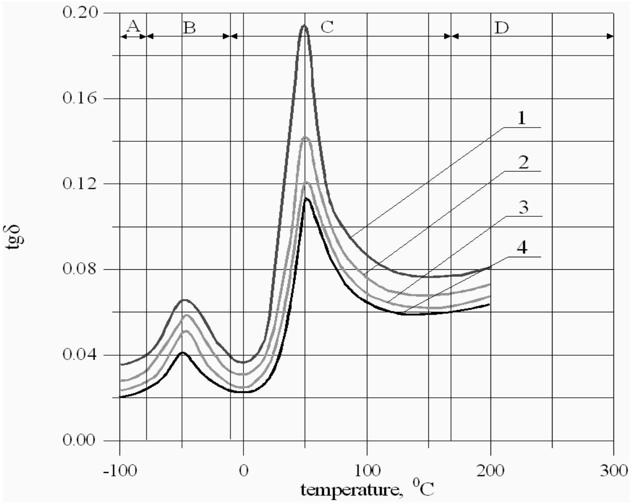

Fig. 3. Values of a loss tangent tgδ in relation to the temperature T, 10 Hz frequancy and glass fibre content before annealing: 1 – polyamide 6, 2 – polyamide 6 + 10%, 3 – polyamide 6 + 30%, 4 – polyamide 6 + 50%. A – elastic deformation range, B – glass transition range, C – viscoelastic deformation range, D – plastic transition range

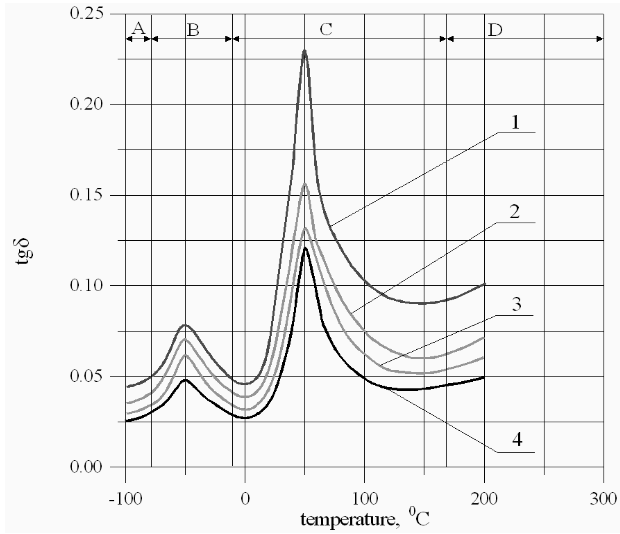

Fig. 4. Values of a loss tangent tgδ in relation to the temperature T, 10 Hz frequancy and glass fibre content after annealing : 1 – polyamide 6, 2 – polyamide 6 + 10%, 3 – polyamide 6 + 30%, 4 – polyamide 6 + 50%. A – elastic deformation range, B – glass transition range, C – viscoelastic deformation range, D – plastic transition range

4. Conclusions

Measurements of dynamical properties are a general – purpose method of examinations of material behaviour under dynamical sinusoidal load. The increase in glass fibre content did not cause essential changes of the form of relationship between modulus of complex number E^*, loss tangent tgδ and the temperature.

These was only the decrease in a real number E' and a loss tangent tgδ. Polymers of a loss tangent in the range tgδ>0.1 are materials of a big ability to vibration damping [1,6,12,13].

The decrease of a loss tangent with the increase of glass fibre content testifies damping properties of examined composites.

For the matrix the loss tangent was about 0.19, but after its filling with 50% glass fibre it decreased to 0.1.

When the glass fibre content increases then a real number, responsible for energy accumulation and restoring during successive deformation cycles, increases and values of a loss modulus, connected with energy dissipation, decreases.

The increase in filler fibre glass content and the heat treatment didn't cause the significant change in the dependence of the conservative modulus E' and the mechanical loss tangent tgδ vs temperature. The increase in the storage modulus E^* value and the decrease in mechanical loss tangent tgδ was observed.

Polyamide 6 and its fibre glass filled composites after annealing show both the increase in conservative modulus and the mechanical loss tangent coefficient.

Polyamide 6 composites after annealing show 15% increase in the value of the mechanical loss tangent.

The heat treatment in the from of annealing additionally causes increase the conservative modulus value.

References

[1] H. Galina, Physical chemistry. Rzeszow University of Technology, 1998 (in Polsih).

[2] J. Koszul, Polymer materials, Czestochowa University of Technology, 1999 (in Polsih).

[3] J. Koszkul Influence treatment on structure and physical properties polyamide 6 and polyoxymethylene. Scientific Book Czestochowa University of Technology. Mechanical no 21, Czestochowa (1985).

[4] R. Sikora, Plastics. Type, properties and structure. Lublin University of Technology, Lublin, 1991.

[5] A.P. Wilczyński, Fibrous composites polymers. WNT, Warsaw, 1996 (in Polsih).

[6] D. Żuchowska, Solid Polymers. WNT, Warsaw, 1995.

[7] P.V. Joseph, K. Joseph, S. Thomas, C.K.S. Pillai, V.S. Prasad, G. Groeninck, M. Sarkissova, The thermal and crystallisation studies of short sisal fibre reinforced polypropylene composites. Composites, Part A, 34 (2003) 253-266.

[8] J. M. Garcıa-Martınez, O. Laguna, S. Areso, E. P. Collar, A dynamic–mechanical study of the role of succinil-fluoresceine grafted atactic polypropylene as interfacial modifier in polypropylene/talc composites. Effect of grafting degree. European Polymer Journal 38 (2002) 1583–1589.

[9] A. Gnatowski, J. Koszkul, Investigation on PA/PP mixture properties by means of DMTA method. Journal of Materials Processing Technology 175 (2006) 212–217.

[10] N. Chen, Ch. Wan, Y. Zhang, Y. Zhang, Effect of nano-CaCO3 on mechanical properties of PVC and PVC/Blendex blend. Polymer Testing 23 (2004) 169–174.

[11] J.M. Ward: Mechanical Properties of Solid Polymers, PWN, Warsaw, 1975 (in Polsih).
[12] J.F. Rabek, Physical chemistry base. Wroclaw University of Technology Edition, 1977 (in Polsih).
[13] J.D. Ferry, Viscoelastic Properties of Polymers, WNT, Warsaw, 1965.
[14] A.G. Pedroso, D.S. Rosa, Mechanical, thermal and morphological characterization of recycled LDPE/corn starch blends. Carbohydrate Polymers 59 (2005) 1–9.
[15] Ch. Ding, D. Jia, H. He, B. Guo, H. Hong, How organo-montmorillonite truly affects the structure and properties of polypropylene, Polymer Testing 24 (2005) 94–100.
[16] K. Wakabayashi, R.A. Register, Micromechanical interpreta tion of the modulus of ethylene–(meth)acrylic acid copolymers. Polymer 46 (2005) 8838–8845.
[17] M.B. Saeed, Mao-Sheng Zhan, Effects of monomer structure and imidization degree on mechanical properties and viscoelastic behavior of thermoplastic polyimide films. European Polymer Journal 42 (2006) 1844–1854.