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DMTA AND DSC ANALYSES OF COMPOSITE PA 6,6 WITH GLASS FIBRE AFTER DYE ADDITION AND AGEING

Determination of the influence of a dye addition and electrochemical ageing on the change of dynamic mechanical properties, investigated by the DMTA method for samples made of polyamide 6,6 composite with glass fibre was the aim of this work. Using this equipment, the dynamical properties of polyamide 6,6 composite in relation to the temperature and frequency were determined. The samples were bended with a frequency of 1 Hz and 10 Hz in a temperature range from –50 to 160°C and a heating rate of 2 K/min. A decrease of the value storage modulus for PA 6,6 with a content of 25% of glass fibre addicion after ageing was observed. A similar dependence was obtained for samples with dye addition. A similar dependence also was obtained for the frequency 1 and 10 Hz. With an increase of temperature, the storage modulus decreases. It was found, that after electrochemical ageing, the value of tanδ decreases. Investigation of the crystallinity degree using the DSC method as well as the investigation of the structure using optical microscopy have been made. The DSC investigations prove the decrease in the crystallization degree of PA 6,6/glass fibre composite for the samples with ageing and dye addition. The investigation results provide information about dyed PA 6,6/glass fibre composite behaviour after ageing, which can be useful in practice, when selecting the material for parts that will have to work in conditions of electrochemical ageing.

Keywords: composites, dynamic properties, thermal properties, structure, polyamide 6,6, glass fibre, dye, ageing

ANALIZA DMTA I DSC KOMPOZYTU PA 6,6 Z WŁÓKNEM SZKLANYM PO DODANIU BARWNIKA I PROCESIE STARZENIA

Wytwarzanie kompozytów poliamidu jest uzasadnione licznymi zaletami metod ich wytwarzania, możliwości przeprowadzenia mieszania podczas przetwórstwa, rozszerzonymi możliwościami ich wykorzystania i warunkami eksploatacji. Starzenie kompozytów pociąga za sobą zmianę właściwości termomechanicznych i struktury tych materiałów. Przewidywanie zmian właściwości na skutek starzenia odgrywa dużą rolę w planowaniu składu, a także w sporządzaniu kompozytów polimerowych. W artykule omówiono wyniki badań wpływu dodatku barwnika oraz starzenia na wybrane właściwości kompozytu poliamidu 6,6 o zawartości 25% włókna szklanego. Badania obejmowały: właściwości termomechaniczne, analizę termiczną oraz strukturę nadcząsteczkową. Właściwości termomechaniczne określono metodą DMTA. Wyznaczono przebiegi zmian wartości modułu zachowawczego E' oraz tangensa kąta stratności mechanicznej tgδ w zależności od temperatury i częstotliwości drgań. Zbadano stopień krystaliczności metodą DSC oraz strukturę z użyciem mikroskopu optycznego w świetle przechodzącym. Badania przeprowadzono dla kompozytu poliamidu 6,6 z 25% zawartością włókna szklanego o nazwie firmowej Vampamid 66 2526 V0 Naturale 30. Określono wpływ starzenia elektrochemicznego na badane właściwości zarówno kompozytu, jak i kompozytu z dodatkiem barwnika. Zaobserwowano zmiany wartości modułu zachowawczego i tangensa strat mechanicznych w funkcji temperatury oraz częstotliwości drgań dla próbek po procesie starzenia. W przeprowadzonych badaniach zarejestrowano najmniejsze wartości modułu zachowawczego dla kompozytów po procesie starzenia elektrochemicznego zarówno dla kompozytów bez, jak i z dodatkiem barwnika. Charakter zmian wartości modułu zachowawczego w funkcji temperatury jest jednakowy dla badanych częstotliwości drgań 1 i 10 Hz. Zarejestrowano wpływ procesu starzenia na stopień krystaliczności, którego wartość jest mniejsza dla próbek badanego kompozytu starzonego i z dodatkiem barwnika.

Słowa kluczowe: kompozyty, właściwości dynamiczne, właściwości termiczne, poliamid 6,6, włókno szklane, barwnik, starzenie

INTRODUCTION

The range of using polymer materials can be broadened by chemical or physical modification. The chemical modification of polymers takes place during polymer production, whereas the physical modification of polymers consists in their filling with powder or fiber fillers. Constructional polymer composites have good mechanical properties and resistance to many physical, chemical and biological factors. The properties of constructional polymer composites allow their wide use in the production of structural components of different machines and devices. The properties of polymeric materials depend on the structural factors of the polymer as well as on the conditions of exploitation [1-7]. The structural factors are for example: molecular weight, chemical structure of macromolecules, and physical structure of the polymer chain, crystallinity, molecular orientation and presence of additives. The following factors belong to the conditions of exploitation: temperature, time of load, pressure, kind of deformation etc. [3-11]. The aim of this investigation was to determine the influence of electrochemical ageing on the thermomechanical properties and structure of dyed PA6,6/glass fiber composite. The notion "degradation" or "ageing" is used to describe the changes in the physical properties of polymer materials, caused by chemical, thermal, biological, mechanical or photochemical reactions that lead to breakage of the macromolecule chain. Chemical degradation means the processes caused by chemical reagents: acids, solvents, bases etc. The solubility of polymers in solvents is usually compatible with their chemical constitution. Polymers contain polar groups dissolved in polar solvents. Most polymers cannot be dissolved in water, but can only be absorbed, which causes swelling of the polymers. The application of polymers in a natural environment requires selection of the proper kind of polymer, depending on the corroding medium, temperature and stress occurring in the material [4, 5, 12]. The results of dynamic and thermal properties testing as well as the structure of the tested composite before and after the process of electrochemical ageing are presented in this paper.

MATERIALS, APPARATUS AND INVESTIGATION METHODOLOGY

Polyamide 6,6 composite with 25% glass fiber, trade name Vampamid 66 2526 V0 Naturale 30, with an addition of dye Lifocolor - Red 31580F PE (manufacturer: Lifocolor Farben GmbH & Co. KG) was used for the investigation. The samples for testing were injected using a KraussMaffei KM65-160C1 injection moulding machine, with a screw of 30 mm in diameter, three heating zones, L/D = 23 and constant pitch. The clamping force of the machine is 650 kN. The optimal properties of the injected samples were obtained in following processing conditions: pressure limit in plasticizing unit: 100 MPa, holding pressure: 45 MPa, holding time: 20 s, cooling time: 15 s, melt temperature: 280°C, mould temperature: 100°C. Tests were made for PA 6,6/glass fiber composite and for PA 6,6/glass fiber composite with a 2% dye addition. Electrochemical ageing was conducted in a water solution of NaCl, 25% concentration and pH 8, where the samples for testing were put. An electrolyze process with the following parameters was conducted: direct current, with intensity of 0.3 A, voltage of 4.3 V, time 720 h. Tests of thermomechanical properties were made with the use of a DMA 242 apparatus, manufactured by Netzsch, with a holder for free three-point bending of beam-shape samples.

The samples of the PA6,6/glass fiber composite put in the holder were subjected to sinusoidally-changed force, at the frequency of 1 and 10 Hz, with a constant amplitude and by heating the sample from a temperature of −50°C up to 160°C. The thermal properties were investigated using the DSC method and structure using an optical microscope, in transmitted light. The DSC tests were done with the use of a scanning microcalorimeter PC 200, produced by Netzsch. The DSC curves were acquired during heating the samples at a heating rate of 10°C/min, within a temperature range from 50 up to 300°C. In order to minimize the skin-core effect, the samples were cut parallel to the molten polymer flow direction in an injection mould cavity. The software of the DSC apparatus was used to calculate the crystallinity degree. The software allows investigation of the melting process of the sample in the considered temperature range and calculation of the area between the thermographic curve and base line in the endothermic peak temperature range. The mass of the samples was in the range of 7 to 9 mg. The samples were weighed using scales produced by SARTORIUS, with an accuracy of 0.01 mg and with self-calibration and closed measurement chamber. Investigation of the polymer structure was conducted with the use of an optical microscope Nikon Eclipse E 200. The samples were microtomed slices, with a thickness of 12÷18 μm, that were cut from the core of the injection moulded parts used for DMTA tests.

RESULTS OF INVESTIGATION AND DISCUSSION

The results of the DMTA investigations of a polyamide with glass fibre composite before and after ageing were presented in the form of a graph showing the course of the storage modulus E' and mechanical loss tangent tgδ in relation to temperature (Fig. 1). The thermomechanical curves obtained during the DMTA tests for the composite with 2% dye addition - before and after electrochemical ageing - were presented in Figure 3.

The performed test showed that the addition of dye in the composite causes a decrease in the mechanical loss factor. The analysis of the registered values of the storage modulus and mechanical loss factor shows the differences for the material before and after electrochemical ageing. The plots of the registered values are presented in Figures 1b) and 2b). In the range of temperature values lower than the glass transition temperature, the composite of polyamide with glass fiber is in a glassy state, is hard and brittle. With the increase of temperature, the values of the modulus for composite polyamide 6,6/glass fiber decrease less than the composite with the dye addiction. Electrochemical ageing caused a decrease in storage modulus values.

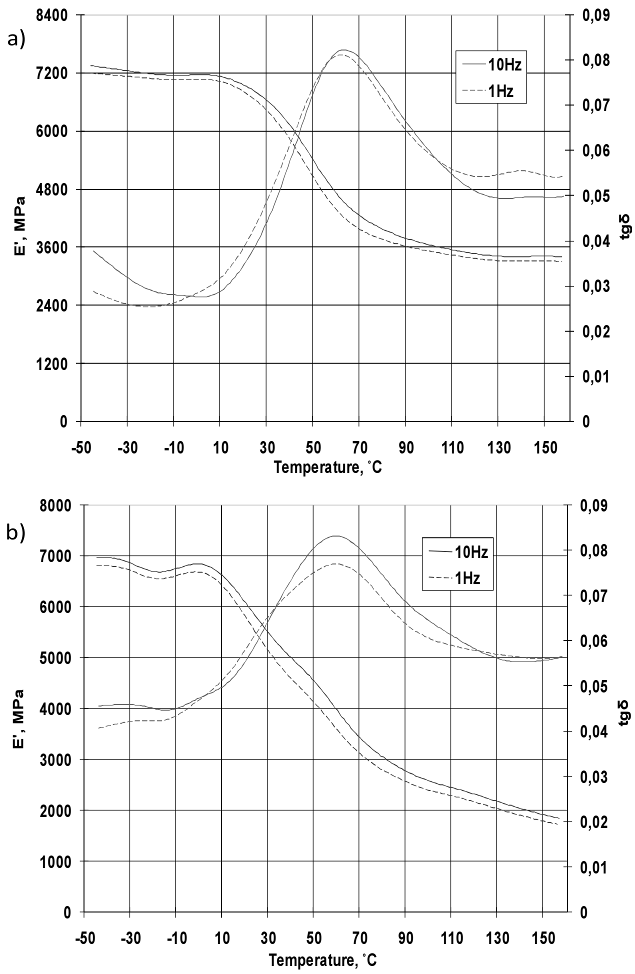


Fig. 1. Dependence of storage modulus value and mechanical loss tangent vs. temperature of polyamide 6,6 composite with glass fibre: a) before ageing, b) after ageing

Rys. 1. Zależność modułu zachowawczego i współczynnika stratności mechanicznej od temperatury kompozytu PA 6,6 z włóknem szklanym: a) przed starzeniem, b) po starzeniu

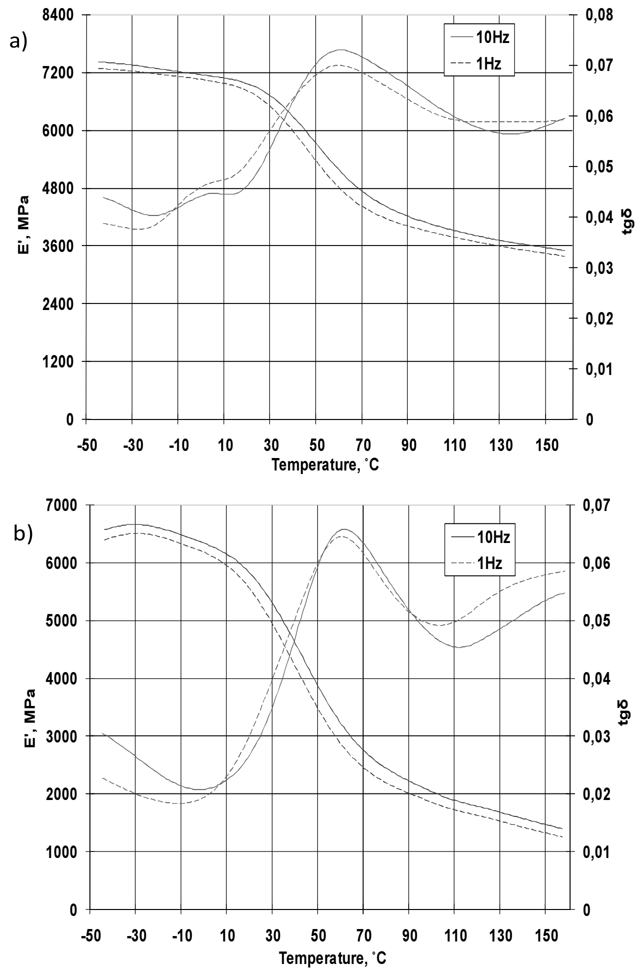


Fig. 2. Dependence of storage modulus value and mechanical loss tangent vs. temperature of polyamide 6,6 composite with glass fibre: a) with dye addition, b) with dye addition after ageing

Rys. 2. Zależność modułu zachowawczego i współczynnika stratności mechanicznej od temperatury kompozytu PA 6,6 z włóknem szklanym: a) z dodatkiem barwnika, b) z dodatkiem barwnika po starzeniu

The DSC thermograms for composite PA6,6/glass fiber and composite PA6,6/glass fiber with dye addition before and after electrochemical ageing are presented in Figure 3. The values calculated on the basis of the DSC thermographic curves were listed in Table 1. As a result of electrochemical ageing of the PA6,6/glass fiber composite, the crystallinity degree value of the composite decreased. The reason for such a change in the values is a decrease in molecular weight caused by macromolecule cracking. The degree of chain branching and molecular weight distribution significantly influence the crystallinity of the composite, which is a significant factor that impacts the performance properties of this material. The lowest values were obtained for the composite with dye addition after electrochemical ageing. The process of crystallization is influenced by dye. The glass fiber and small amount of dye in powder - form and its orientation along the flow direction within the injection mould cavity can cause a decrease in the crystallinity degree values.

TABLE 1. **Results of DSC investigations**
TABELA 1. **Wyniki badań metodą DSC**

Samples	Crystallinity degree [%]	Melt temperature range [ºC]	Melt temperature - peak maximum [ºC]
PA 6,6 + 25% glass fibre	17.2	243.3÷274.4	266.1
PA 6,6 + 25% glass fibre after electrochemical ageing	16.4	243.6÷273.3	264.1
PA 6,6 + 25% glass fibre with dye addition	15.1	247.2÷269.2	263.2
PA 6,6 + 25% glass fibre with dye addition after electrochemical ageing	13.6	249.1÷276.2	263.3

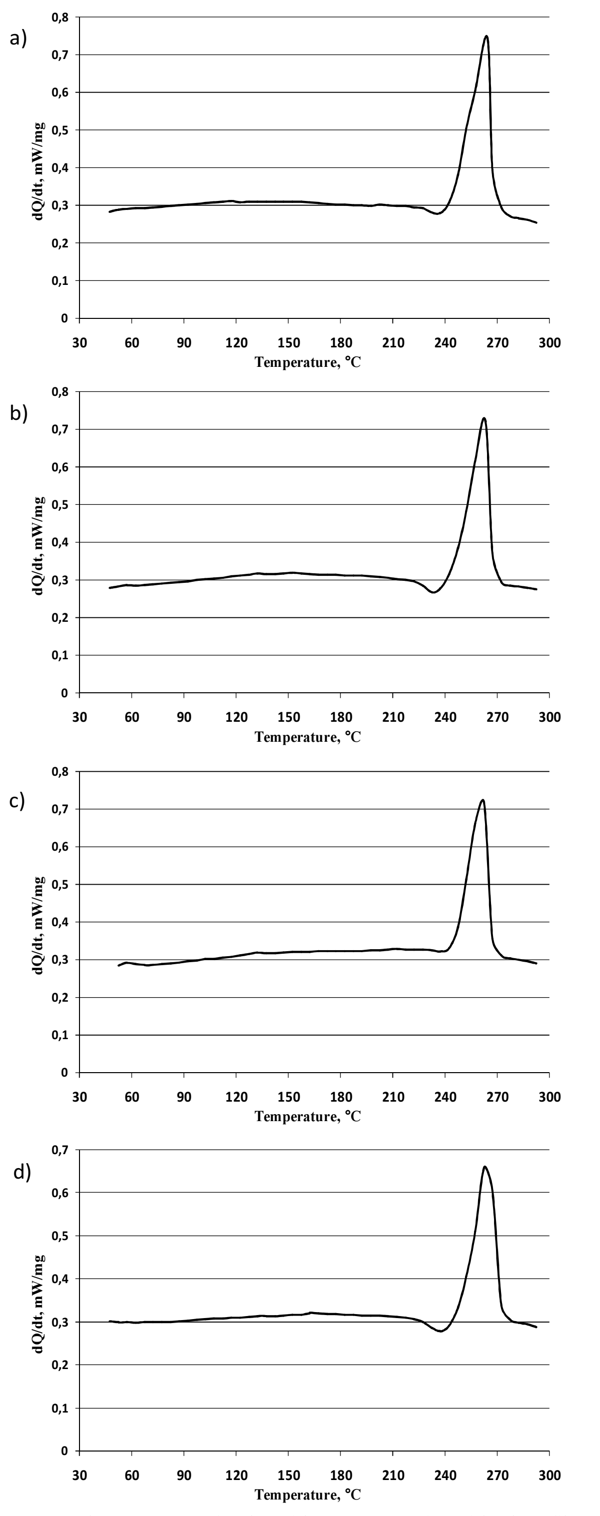
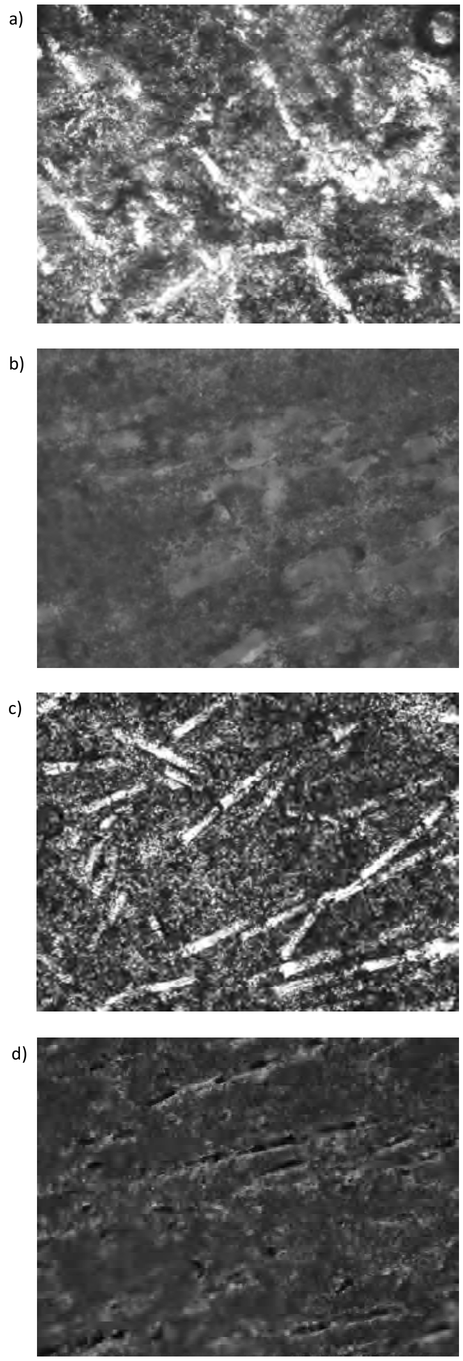


Fig. 3. DSC thermograms of polyamide 6,6 composite with glass fibre: a) before ageing, b) after ageing, c) with dye addition, d) with dye addition after ageing

Rys. 3. Termogramy DSC: kompozytu PA 6,6 z włóknem szklanym: a) przed starzeniem, b) po starzeniu, c) z dodatkiem barwnika, d) z dodatkiem barwnika po starzeniu

This decrease is caused by the probability of intermolecular reactions in the polymer leading to a lower creatation of crystallization nuclei during the cooling down of the composite with dye. For the composite samples, as a result of the ageing process, the range of melting temperature did not change significantly but the temperature of the highest melting rate was reduced. In the case of the composite with dye, a lower value of melting peak maximum temperature was recorded and the shift of the melting temperature ranged towards higher temperature values for the composite samples with dye after ageing. The investigation of the composite structure using the optical microscope showed changes between the composite before and after electrochemical ageing (Fig. 4).



Rys. 4. Struktura obserwowana pod mikroskopem optycznym przy powiększeniu 350x kompozytu PA 6,6 z włóknem szklanym: a) przed starzeniem, b) po starzeniu, c) z dodatkiem barwnika, d) z dodatkiem barwnika po starzeniu

Fig. 4. Structures observed with optical microscope with magnification of 350x of polyamide 6,6 composite with glass fibre: a) before ageing, b) after ageing, c) with dye addition, d) with dye addition after ageing

In the case of the composite without dye, small-sized and well-visible shape spherulites occur. In the case of the composite with dye addition, a decrease in size, and after ageing - a decrease in the quantity of structural elements was also noticed.

CONCLUSIONS

The properties of the composite depend on the presence of dye. The lowest values of storage modulus were recorded for the composite after electrochemical ageing. The highest values of loss factor were recorded during testing the composite without dye. It was noticed that the curves of storage modulus - all of them: for the composite and composite with a dye, before and after electrochemical ageing process are close to each other but their maximum values differ. A significant influence of electrochemical ageing on the thermal properties and structure of the investigated composite was noticed. On the basis of the DSC tests, a decrease in the crystalline phase of the composite for samples after ageing and a decrease for the samples with a dye after ageing appeared. Moreover, the range of melting temperature changed.

REFERENCES

[1] Sterzyński T., Śledź I., Jednopolimerowe kompozyty polipropylenowe - wytwarzanie, struktura, właściwości, Polimery 2007, 6, 443-452.

[2] Pramoda K.P., Liu T., Effect of moisture on the dynamic mechanical relaxation of polyamide-6/clay nanocomposites, J. Polym. Sci., Part B: Polym. Phys. 2004, 42, 10, 1823--1830.

[3] Mazurkiewicz S., Porębska R., Próba oceny jakości struktury kompozytów za pomocą pierwszych obciążeń cyklicznych, Czasopismo Techniczne Mechanika, Wydawnictwo Politechniki Krakowskiej 2004, 13, 85-92.

[4] Kelar. K., Modyfikacja polimerów, Wydawnictwo Politechniki Poznańskiej, Poznań 1992

[5] Żuchowska D., Polimery konstrukcyjne, wyd. II, WNT, Warszawa 2000.

[6] Gnatowski A., Koszkul J., Investigations of the influence of compatibilizer and filler type on the properties of chosen polymer blends, Journal Material Processing Technology 2005, 52-58, 162-163.

[7] Kwiatkowska M., Broza G., Męcfel J., Sterzyński T., Rosłaniec Z., Otrzymywanie i charakterystyka nanokompozytów polimerowych PBT/nanorurki węglowe, Kompozyty (Composites) 2005, 2, 5, 3-15.

[8] Gnatowski A., Influence of the polyvinylpyrrolidone modification on crystallines and properties of selected thermoplastic polymers, Journal of Polymer Engineering 2007, 27, 6-7, 507-524.

[9] Campoy J., Arribas J.M., Zaporta U.M., Crystallization kinetics of polypropylene-polyamide compatibilized blends, European Polymer Journal 1995, 31, 5, 475-480.

[10] Jakubowska P., Sterzyński T., Samujło B., Badania reologiczne kompozytów poliolefinowych o wysokim stopniu napełnienia z uwzględnieniem charakterystyk p-v-T, Polimery 2010, 5, 379-389.

[11] Manning S.C., Moore R.B., Reactive compatibilization of polypropylene and polyamide-6,6 with carboxylated and maleated polypropylene, Polymer Engineering and Science 1999, 39/10, 1921-1926.

[12] Göpferich A., Mechanisms of polymer degradation and erosion, Biomaterials 1996, 17, 2, 103-114.

