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Performance properties and structure of electrochemically aged polypropylene with a dye addition

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ABSTRACT

Purpose: Determination of the influence of a dye addition and electrochemical ageing on the change of dynamic mechanical properties, investigated by DMTA method for samples made of polypropylene was the aim of this work. The investigation of crystallinity degree using DSC method as well as the investigation of the structure using optical microscopy have been made. Hardness by ball indentation method, Shore hardness, Vicat softening point and water absorptivity were tested.

Design/methodology/approach: Investigation using DMTA method was carried out for samples subjected to one-axial bending. The change in the value of the storage modulus E' and the mechanical loss factor (tangent δ) in function of the temperature and oscillation frequency in DMTA tests were determined. In order to verify the change of thermal properties of PP with 2% of dye addition, before and after electrochemical ageing, the investigation using DSC method was made.

Findings: Higher values of the storage modulus occurred for the samples with dye addition. The crystallinity degree values were lower for the samples after electrochemical ageing. It was found that electrochemical ageing results in decrease in hardness values and Vicat softening temperature while increase in water absorptivity was noticed.

Research limitations/implications: Dynamic properties of polypropylene with the dye addition were determined in one-axial bending test. In real application, the parts manufactured from this material can be subjected to more complex load.

Practical implications: The investigation results let know about dyed polypropylene behaviour after ageing, what can be useful in practice, when selecting the material for parts that will have to work in conditions of electrochemical ageing.

Originality/value: In order to estimate the polymer behaviour in different thermal conditions, dependences of the storage modulus and the mechanical loss factor were determined in function of temperature in one-axial bending.

Keywords: Engineering polymers, Mechanical properties, Thermal properties

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METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

1. Introduction

Properties of polymeric materials depend on structural factors of polymer as well as on conditions of exploitation. The structural factors are for example: molecular weight, chemical structure of macromolecules, and physical structure of 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. [1-8].

Technical and economical usability of polymeric materials depend on how they will meet the requirements regarding stiffness and strength to reach the sufficient durability in exploitation conditions. The traditional mechanical characteristics, obtained as the results of tests made by static load - tensile, compression and torsion, are not sufficient to forecast the behaviour of these materials in extreme exploitation conditions, as well as after long time of exploitation. It is therefore problematic to choose the proper testing methods that will allow forecasting the change in viscoelastic properties in function of time, on the base of experimental data [1-6]. Since polymeric materials are characterized by viscoelastic properties, all their physic mechanical properties depend not only on time but also on temperature. Methods of these materials testing should therefore have these relations taken into account.

One of the testing methods is thermal analysis of dynamical mechanical properties (DMTA). It is used for measurements of relaxation modules in function of time in constant temperature and in function of load change frequency and temperature [9-16]. Mechanical characteristics obtained as results of tests made with static load in room temperature are not sufficient to forecast the material behaviour in particular conditions of use and long time periods. [10-16]. In order to characterize fully the properties of tested materials and evaluate, how they will behave in forecasted conditions of use, it is necessary to learn the time and temperature dependences of the relaxation modules, expressed by viscoelastic functions.

The way of load used in experimental measurements, changed according to sinusoidal function, is often similar to the schemes of load occurring in practical applications of polymeric materials. Thermal analysis of dynamical mechanical properties (DMTA) is one of methods used for evaluation of the changes occurring in polymeric materials in a wide range of temperature and load change frequency. As the result of this analysis the functions of dynamical Young modules and mechanical loss tangent are obtained. The knowledge of these functions allows determining the relations between molecular parameters and mechanical properties of polymeric materials [17-26].

The aim of this investigation was determination of the electrochemical ageing influence on the chosen properties of dyed polypropylene. The notion “degradation” or “ageing” is used for description of changes in physical properties of polymers, caused by chemical, thermal, biological, mechanical or photochemical reactions that lead to break of macromolecule chain. Chemical degradation means the processes caused by chemical reagents: acids, solvents, bases etc. Solubility of polymers in solvents is usually compatible with their chemical constitution. Polymers containing polar groups dissolved in polar solvents. Most of the polymers cannot be dissolved in water, but only can be absorb, what causes swelling of polymers [2, 3]. Application of polymers in natural environment requires selection of proper polymer kind, dependent on corroding medium, temperature and stress occurring in material. The results of dynamic and thermal properties testing as well as structure of the tested materials before and after process of electrochemical ageing were presented in this paper.

2. Materials and investigation methodology

Polypropylene Moplen HP 501 H, manufactured by Basell, with addition of dye Lifocolor-Green 47145F PE (manufacturer: Lifocolor Farben GmbH & Co. KG) was used for the investigation.

The samples for testing were injected using KraussMaffei KM65-160C1 injection moulding machine, with the screw of 30 mm diameter, three heating zones, L/D=23 and constant pitch. The clamping force of the machine is 650 kN. Optimal properties of injected samples were obtained at following processing conditions:

- pressure limit in plasticizing unit: 70 MPa
- holding pressure: 35 MPa
- holding time: 20s
- cooling time: 15 s
- melt temperature: 230°C
- mould temperature: 45°C.

Tests were made for polypropylene and for polypropylene with 2% dye addition. Electrochemical ageing was conducted in water solution of NaCl, 25% concentration and pH 8 where the samples for testing were put. 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 dynamic mechanical properties were made with the use of DMA 242 apparatus, manufactured by NETZSCH, with a holder for free three-point bending of beam-shape samples (Fig. 1).

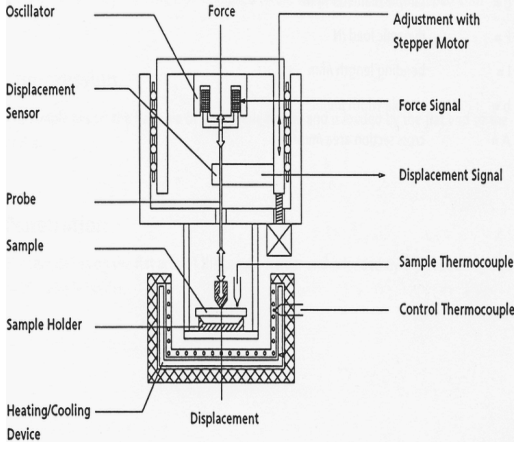


Fig. 1. The scheme of the apparatus for three-point bending of samples

The samples put in the holder were subjected to sinusoidally-changed force, at the frequency of 1Hz and 10 Hz, with constant amplitude and with heating the sample from temperature -50°C up to 160°C.

Thermal properties were investigated using DSC method and structure - using optical microscope, in transmitted light.

DSC tests were done with the use of scanning microcalorimeter PC 200, produced by Netzsch. DSC curves were acquired during heating the samples at the heating rate of 10°C/min, within temperature range from 20 up to 220°C. In order to minimize skin-core effect the samples were cut parallel to molten polymer flow direction in injection mould cavity. The software of DSC apparatus was used to calculate crystallinity degree. The software allows investigating melting process of the sample in the considered temperature range and calculation of the area between thermographic curve and base line in the endothermic peak temperature range. Mass of the samples was in the range 7 to 10 mg. The samples were weighted using scales produced by SARTORIUS, with the accuracy of 0.01 mg and with self-calibration and closed measurement chamber.

The investigations of the other properties have been also conducted, i.e. hardness with the ball indentation tester and Shore hardness tester, the softening temperature point according to Vicat method with the HAAKE N8 machine and water absorptivity tests, according to the present standards.

Investigation of polymer structure was conducted with the use of optical microscope Nikon Eclipse E 200. The samples were microtomed slices, with thickness of 10-18μm, that were cut from the core of injection moulded parts used for DMTA tests. Rotary microtome Thermo Shandon Finesse Me+ was used for this purpose.

3. Results of investigation and discussion

Thermomechanical curves obtained during DMTA tests for polypropylene and polypropylene with 2% dye addition – before and after electrochemical ageing - were presented in Fig 2 and 3.

The performed test showed that the addition of dye in polypropylene causes increase of storage modulus E' mechanical loss factor (tanδ). The analysis of registered values of storage modulus and mechanical loss factor shows the differences for material before and after electrochemical ageing. The plots of registered values are presented in Fig 2b) and 3b). In the range of temperature values lower than glass transition temperature polypropylene is in glassy state, is hard and brittle. In glassy state thermal energy is not sufficient to overcome potential barrier for movements and rotations of macromolecule segments. The system is in the state of thermodynamical unbalance. With the increase of temperature the values of modulus for PP decrease. The material is in the range of glass transition, where loss tangent reaches maximum value in glass transition temperature, at deformation frequency of 1 and 10 Hz. In glass transition range a start of Brown motions in macromolecular chain occurs. Thermal energy becomes comparable with the barrier of potential energy for chain rotation. In the contiguity of glass transition temperature viscoelastic properties change very fast with the time and with the temperature. Glass transition temperature is dependent on chemical and molecular structures of polymer that depend on the kind and quantity of filler used in the composite. With the increase of temperature polypropylene passes to high-plastic state. The highest values of storage modulus were registered for PP with dye addition.

Storage modulus (E') value for polypropylene in the temperature of -44 °C was 3607 MPa, at frequency of 10 Hz. Loss factor tanδ value for polypropylene at the frequency of 10 Hz in glass transition temperature (15.6°C) was 0.082. For polypropylene with dye the increase in storage modulus values up to 4211 MPa at the temperature of -45°C and frequency of 10 Hz is visible. The lower value of loss factor tanδ: 0.078, in glass transition temperature 13.1°C was registered for frequency of 10 Hz.

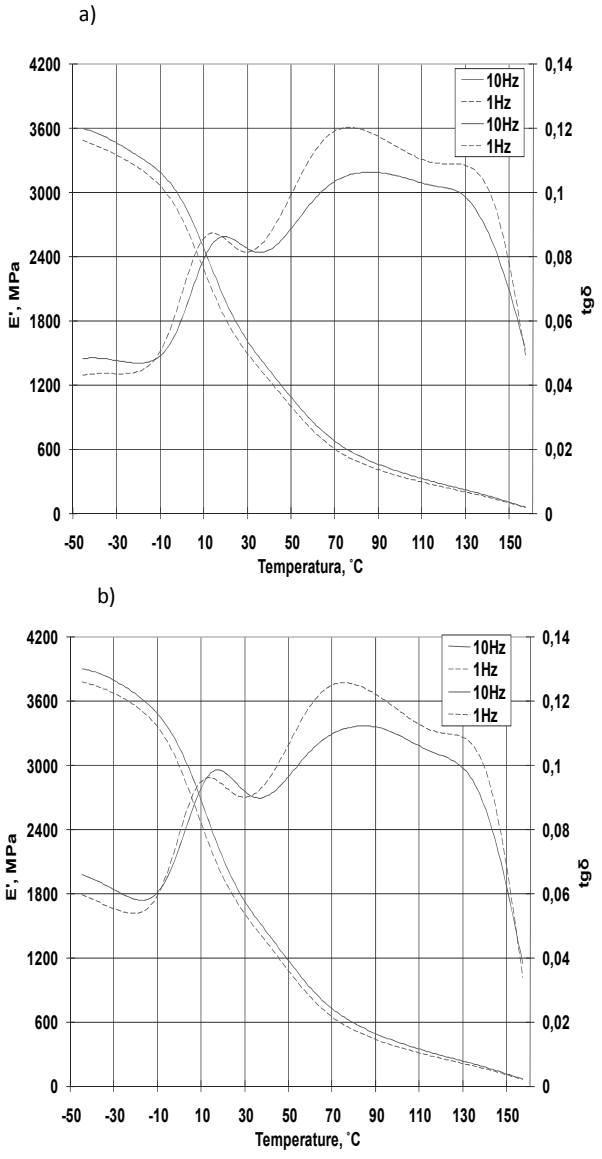


Fig. 2. The dependence of the storage modulus value and mechanical loss factor vs. temperature of: a) polypropylene, b) polypropylene after electrochemical ageing

Electrochemical ageing caused increase in storage modulus values and loss factor values. For polypropylene after ageing the maximum value of E': 3720 MPa in the temperature of -46 °C and maximum value of loss factor tanδ: 0.097 in glass transition temperature 14.3°C, for frequency of 10 Hz were registered. For polypropylene with dye addition higher values of both properties were recorded: storage modulus: 4290 MPa – for frequency of 10 Hz and loss factor: 0.091 in glass transition temperature 12.6°C – for frequency of 10Hz.

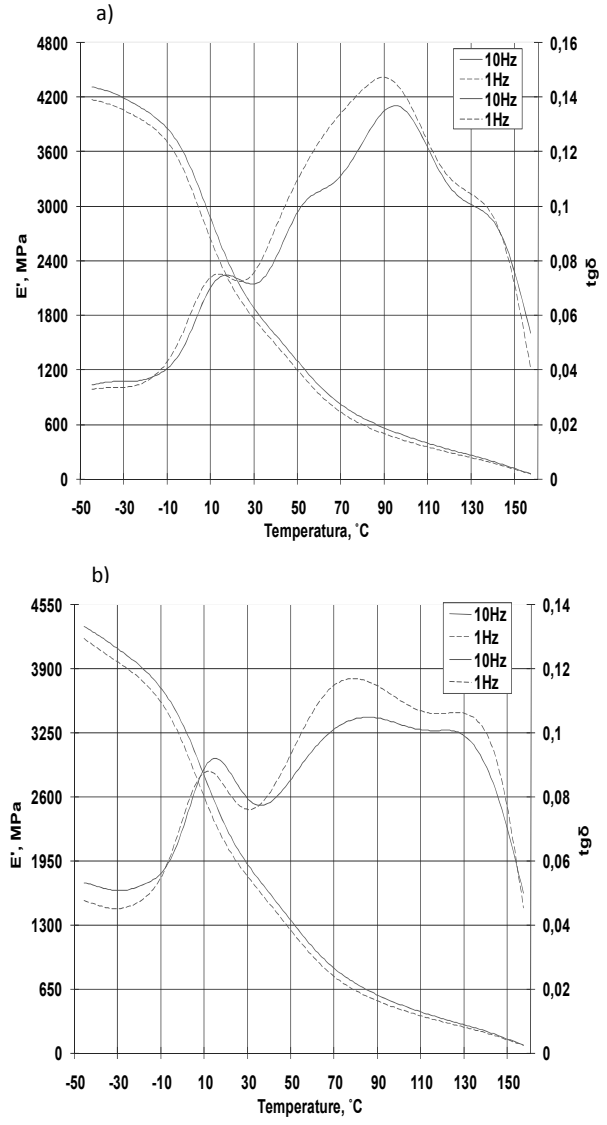


Fig. 3. The dependence of the storage modulus value and mechanical loss factor vs. temperature of: a) polypropylene with dye addition, b) polypropylene with dye addition after electrochemical ageing

DSC thermograms for polypropylene and polypropylene with dye addition before and after electrochemical ageing are presented in Fig. 4 and 5. The values calculated on the base of DSC thermographic curves were listed in table 1.

As the result of electrochemical ageing of polypropylene the crystallinity degree value of polypropylene decreased. The reason of such change in the values is decrease in molecular weight caused by macromolecules cracking. The degree of chain branching and molecular weight distribution influence significantly crystallinity of polypropylene that is a significant factor that impacts performance properties of this material. The highest values were obtained for polypropylene with dye addition. In this case - after ageing process - lower values of crystallinity degree were recorded. Small amount of dye in powder - form and its orientation along flow direction in injection mould cavity can cause the increase in crystallinity degree values. The process of crystallization is influenced by dye. It increases the probability of intermolecular reactions in the polymer leading to create crystallization nucleus while cooling down polypropylene with dye. For polypropylene samples, as a result of ageing process, temperature of highest melting rate was not changed significantly but the range of melting temperature was widen.

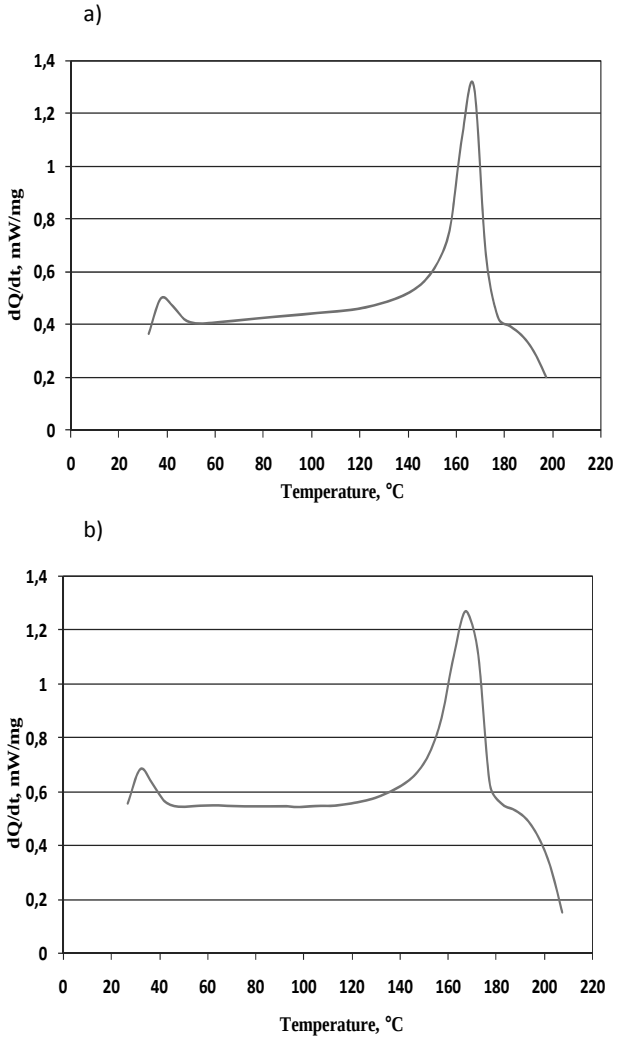


Fig. 4. DSC thermograms of: a) polypropylene, b) polypropylene after electrochemical ageing

In case of polypropylene with dye lower value of melting peak maximum temperature was recorded and the shift of melting temperature range towards higher temperature values for polypropylene with dye samples after ageing. Many authors of papers in this topic [27, 28] claim that crystallinity degree of polymeric material has a significant influence on the value of peak maximum on the curve of loss factor. With decrease of crystallinity degree the curve of mechanical loss factor becomes more similar to curve specific for amorphous polymers.

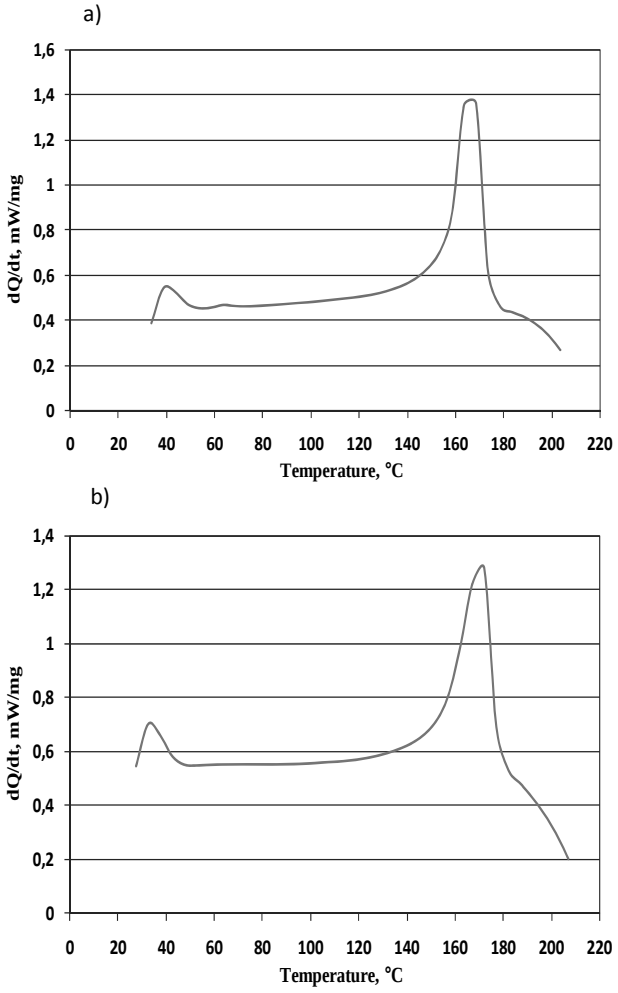


Fig. 5. DSC thermograms of: a) polypropylene with dye addition, b) polypropylene with dye addition after electrochemical ageing

The results of the hardness tests made with the ball indentation tester and Shore tester, softening temperature point according to Vicat method and water absorptivity tests for the investigated materials before and after electrochemical ageing are presented in Fig. 6-9. As the result of electrochemical ageing of polypropylene and polypropylene with the dye addition hardness values and softening temperature point values decreased. After ageing in polypropylene the increase in water sorption appears.

Table 1.
The results of DSC investigations obtained from calculations of Netzch programme

Sample	Crystallinity degree, %	Melt temperature range, °C	Melt temperature - peak maximum, °C
PP	42,1	142.6-176.9	167.6
PP after electrochemical ageing	40,8	136.1-184.1	168.1
PP with dye addition	43.2	138.8-177.68	165.9
PP with dye addition after electrochemical ageing	42.3	142.9-186.4	168.6

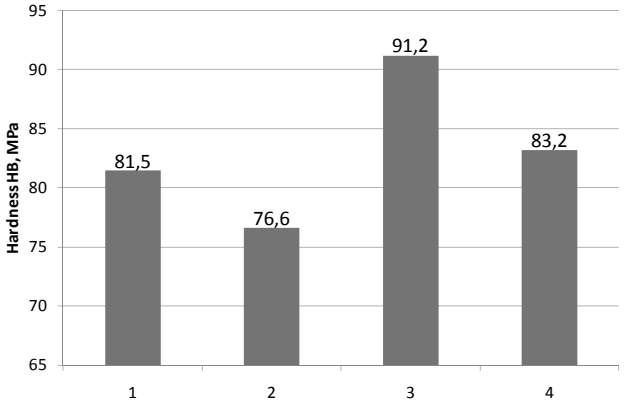


Fig. 6. The results of hardness tests by ball indentation method: (1) polypropylene with dye addition after electrochemical ageing, (2) polypropylene after electrochemical ageing (3) polypropylene with dye addition, (4) polypropylene

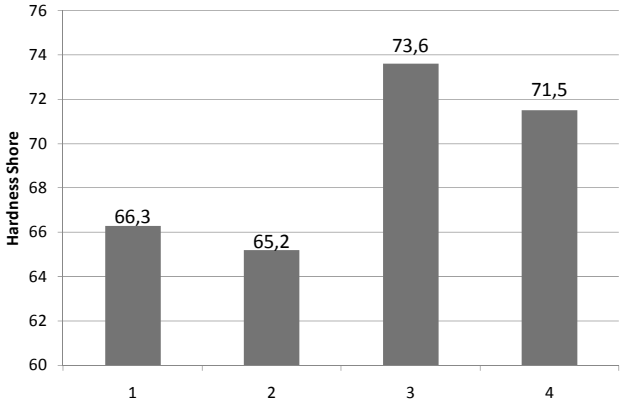


Fig. 7. The results of hardness tests by Shore method: (1) polypropylene with dye addition after electrochemical ageing, (2) polypropylene after electrochemical ageing (3) polypropylene with dye addition, (4) polypropylene

The investigation of polymer structure using optical microscope showed only small changes between polymer before and after electrochemical ageing - Fig. 10.

In case of polypropylene without dye big-size and well-visible shape spherulites occur. In case of polypropylene with dye addition decrease in size, and after ageing - also decrease in quantity of structural elements was noticed.

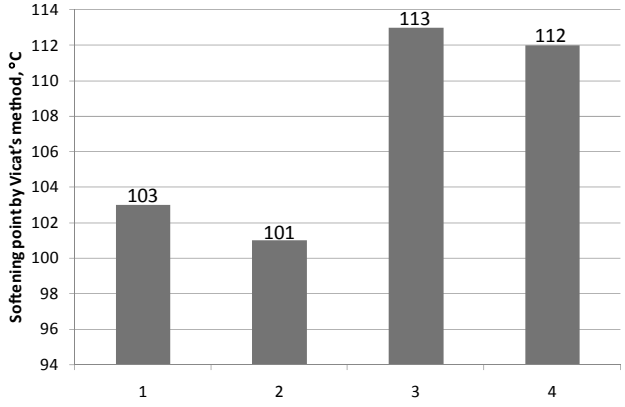


Fig. 8. The results of the softening point tests according to Vicat method: (1) polypropylene with dye addition after electrochemical ageing, (2) polypropylene after electrochemical ageing (3) polypropylene with dye addition, (4) polypropylene

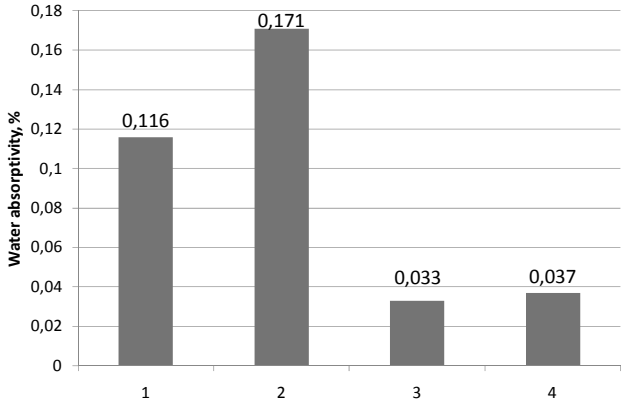


Fig. 9. The results of water absorptivity tests: (1) polypropylene with dye addition after electrochemical ageing, (2) polypropylene after electrochemical ageing (3) polypropylene with dye addition, (4) polypropylene

4. Conclusions

Properties of polymeric material depend on the presence of dye. The highest values of storage modulus were recorded for polypropylene with a dye addition. The highest values of this modulus were obtained for polypropylene after electrochemical ageing.

The highest values of loss factor were recorded during testing the polypropylene with dye.

It was noticed that the curves of storage modulus – all of them: for polypropylene and polypropylene with a dye, before and after electrochemical ageing process are close to each other but their maximum values differ.

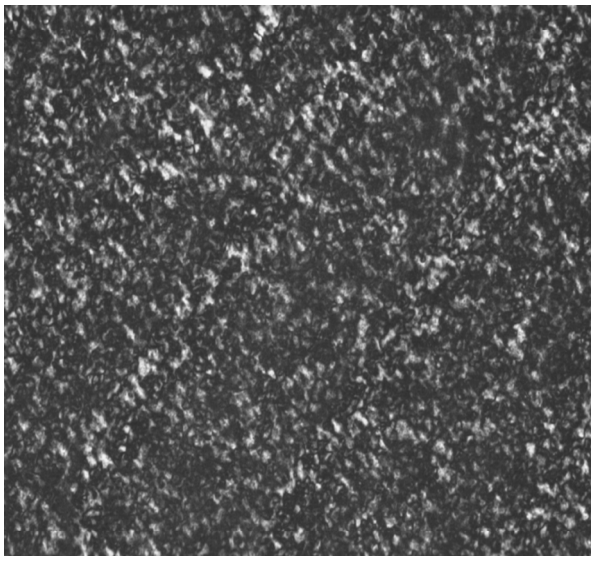
Significant influence of electrochemical ageing on thermal properties and structure of investigated polymeric materials was noticed. On the base of DSC tests the decrease in crystalline phase of polypropylene for samples after ageing and the decrease for samples with a dye after ageing was stated. Moreover, the range of melting temperature changed.

Electrochemical ageing results in decrease in hardness values and Vicat softening temperature while increase in water absorptivity and in size of spherulites was noticed.

a)

b)

c)



d)

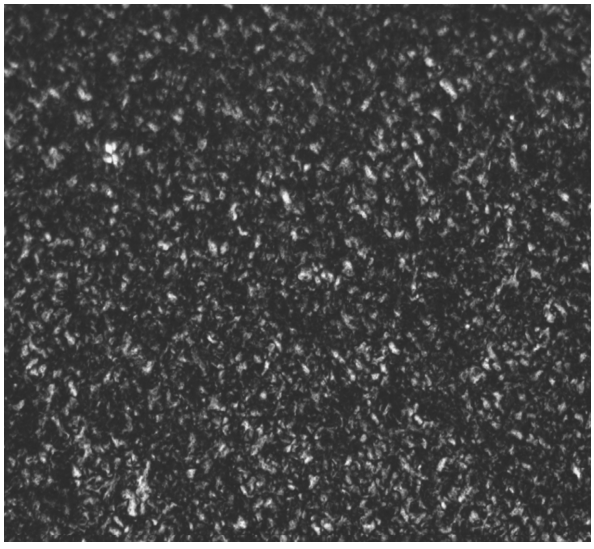


Fig. 10. Structure observed on optical microscope with magnification of 350x: a) PP, b) PP after electrochemical ageing, c) PP with dye addition, d) PP with dye addition after electrochemical ageing

References

[1] J.D. Ferry, Viscoelasticity of Polymers, (1965), WNT, Warsaw (in Polish).

[2] J. Koszkul, Polymeric materials, Publication of Technical University of Czestochowa, 1999 (in Polish).

[3] R. Sikora, Multiparticle plastics. Types, properties and the structure, (1991), Technical University of Lublin (in Polish).

[4] D. Kwiatkowski, Determination of crack resistance on the basis of the J integral for talc filled PP and PA composites, Proceedings of the 13th International Scientific Conference „Achievements in Mechanical and Materials Engineering" AMME'2005, Gliwice - Wisla, 2005, 391–394.

[5] J. Koszkul, E. Bociąga, D. Kwiatkowski, Dynamical properties of polyacetale composites with microspheres from fly - ashes, Polymer Processing Society North American Meeting, Toronto, Ontario, Canada (1998) 72-73.

[6] A. Gnatowski, J. Koszkul, Investigations of the Influence of Compatibilizer and Filler Type on the Properties of Chosen Polymer Blends, Journal of Materials Processing Technology 162-163 (2005) 52-58.

[7] D. Kwiatkowski, J. Nabiałek, A. Gnatowski, The examination of the structure of PP composites with the glass fibre, Archives of Materials Science and Engineering 28/8 (2007) 405-408.

[8] D. Kwiatkowski, J. Nabiałek, P. Postawa, Influence of injection moulding parameters on resistance for cracking on example of PP, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 97-100.

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

[10] J. Koszkul, O. Suberlak, Physical chemistry and polymer properties base, Czestochowa University of Technology Edition, 2001. (in Polish)

[11] J. Nabiałek, D. Kwiatkowski, Investigations of the plastics flow during the injection moulding process - selected results, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 225-228

[12] E. Bociaga, T. Jaruga, Dynamic mechanical properties of parts from multicavity injection mould, Journal of Achievements in Materials and Manufacturing Engineering 23/1 (2007) 83-86.

[13] P. Postawa, A. Szarek, Analysis of changes in bone cement damping factor and its effect on bone load, Journal of Achievements in Materials and Manufacturing Engineering 23/1 (2007) 35-38.

[14] A. Neimitz, Fracture Mechanics. PWN Academic Publishers, Warsaw, 1998 (in Polish).

[15] P. Postawa, D. Kwiatkowski, Residual stress distribution in injection moulded parts, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 171-174.

[16] J. Koszkul, J. Nabiałek, Selected methods of modelling of polymer during the injection moulding process, Journal of Achievements in Materials and Manufacturing Engineering 24/1 (2007) 253-259.

[17] M. Arif Fazal, Numerical prediction of plastic deformation and residual stresses induced by laser shock processing, Journal of Materials Processing Technology 136 (2003) 120-138.

[18] S.B. Singh, S. Ray, Newly proposed yield criterion for residual stress and steady state creep in an anisotropic composite rotating disc, Journal of Materials Processing Technology 143-144 (2003) 623-628.

[19] P. Postawa, A. Szarek, J. Koszkul, DMTA method in determining strength parameters of acrylic cements, Archives of Materials Science and Engineering 28/5 (2007) 309-312.

[20] M.C. Senake Perera, U.S. Ishiaku, Z.A. Mohd. Ishak, Characterisation of PVC/NBR and PVC/ENR50 binary blends and PVC/ENR50/NBR ternary blends by DMA and solid state NMR, European Polymer Journal 37 (2001) 167-178.
[21] A. Gnatowski, J. Koszkul, Investigation on PA/PP Mixture Properties by Means of DMTA Method, Journal Materials Processing Technology 175 (2006) 212-217.
[22] J. Koszkul, J. Nabiałek, Viscosity models in simulation of the filling stage of the injection moulding process, Journal of Materials Processing Technology 157-158 (2004) 183-187.
[23] J. Koszkul, J. Nabiałek, The influence of viscosity model on the results of injection moulding process, Proceedings of the 9th Scientific International Conference „Achievements in Mechanical and Materials Engineering" AMME'2000, Gliwice-Sopot-Gdańsk, 2000, 311-314.
[24] T.D. Papathanasiou, M.R. Kamal, Filling of a Complex-Shaped Mould with a Viscoelastic Polymer. Part I: The Mathematical Model, Polymer Engineering and Science 33 (1993) 400-409.
[25] E. Bociąga, T. Jaruga, J. Koszkul, Plastic Flow Investigation in Multicavity Injection Mould, Proceedings of the 12th International Scientific Conference „Achievements in Mechanical and Materials Engineering" AMME'2003, Gliwice-Zakopane, 2003, 107-110.
[26] R. Sikora, Basics of Polymer Processing, Lublin Polytechnic Publishers, Lublin, 1992, 501.
[27] R.E. Wetton, R. De Blok, P.J. Corish, Research of mixtures of polymers and influences between components of these mixtures with the method of the thermal analysis of dynamic mechanical properties (DMTA), Polimery (1990) 163-166 (in Polish).
[28] J. Zawadzki, Problems of the strain and the fatigue of polymers as constructional materials, (1978), PWN, Warsaw (in Polish).