

The influence of maintenance liquids' absorbance used in the automotive industry on the mechanical properties of polyamide-6/montmorillonite nanocomposites

Tomasz M. Majka^{1,*}, Marcin Majka²

¹Faculty of Chemical Engineering and Technology; Department of Chemistry and Technology of Polymers; Cracow University of Technology

²Faculty of Physics, Mathematics and Computer Science; Cracow University of Technology

E-Mails: tomasz.m.majka@gmail.com; 1392359@gmail.com;

* Author to whom correspondence should be addressed; Tel.: +48-500-567-355;

Abstract: In the present work, an upper limit of absorbance of demineralized water, antifreeze, windscreen washer fluid, brake fluid, gasoline and 15 wt% saline solution, on the polyamide-6 nanocomposites' samples containing 3 wt% montmorillonite (PA-6 / MMT) was determined. The results were compared to the values obtained for pure nylon-6. The comparison allowed to evaluate the applicability of PA-6/MMT nanomaterials with potentially improved barrier properties for creating applications used in the automotive industry.

Keywords: maintenance liquids, nanocomposites, polyamide-6;

1. Introduction

Materials which are defined as polymer nanocomposites are those in which a polymer constitutes the continuous phase (matrix) whereas a nanofiller, featuring at least one dimension in a nanometric scale, forms the dispersed (dispergated) phase. In research which has been carried out so far on polymer nanocomposites, most of the known thermoplastic macromolecular compounds were used as the polymer matrix [1-3]. Among these matrixes, there exists a narrow group of polymers which distinguish themselves for higher mechanical strength and are referred to as engineering polymers. These are: polypropylene, polycarbonate, polyamide, poly(methyl methacrylate), and polyoxymethylene. These chemical compounds are used to produce highly sophisticated applications and industrial structures [3-4]. On the other hand, the nanofillers that are currently used can be divided with regard to their structure into the following three groups [4]:

- monodimensional nanofillers (1D) – carbon nanofibres or nanotubes;
- bi-dimensional nanofillers (2D) – phyllosilicates, graphenes;
- three-dimensional nanofillers (3D) – soot, silica, metal oxides.

In the polymer technology, montmorillonite (MMT) representing phyllosilicates, rocks which occur also in Poland, is widely studied and also practically used. Montmorillonite is built of packets of layers having a 2:1 type three-layered crystallographic structure which contains one octahedral layer sandwiched between 2 tetrahedral layers. The charge of MMT layers is negative and balanced with cations situated between the layers [4-7]. The packet layer is approximately 1 nm thick. The important engineering procedure is organophilization of the surface of the aluminosilicate layers, the purpose of which is to move the layers apart and increase the level of the MMT surface hydrophobicity. Therefore, mainly the organic cations are used, e.g. quaternary ammonium salts [8-9]. The so prepared montmorillonite can be used as an appropriate component to produce polymer nanocomposites by the following methods [4-9]:

- Dispersion and adsorption – the modified montmorillonite is dispersed in a solvent in which the polymer is also solved. In the solvent environment, the nanofiller undergoes the processes of intercalation (inclusion of an organic substance between the packet layers) and/or exfoliation (the total loss of the layered structure and the nanofiller platelets are split by the polymer chains) whereas the macromolecular compound situates itself on the surface and penetrates the aluminosilicate inter-packet layers. In the next stage, the solvent vapours and the polymer/montmorillonite nanocomposite is formed;
- Intercalated polymerisation *in situ* – the modified montmorillonite is dispersed in liquid monomer or prepolymer, after which the monomer is polymerised or the prepolymer chain is extended. The used initiators or catalysts also diffuse to interlayer spaces where they first initiate and then speed up the *in situ* polymerisation process;
- Intercalation in the melted state – in this method, the modified montmorillonite is dispersed in a hot melt of polymer in the processing conditions. Under the influence of shearing forces and temperature, the montmorillonite layers undergo intercalation and/or exfoliation in the thermoplastic polymer matrix. The process takes place in a twin-screw extruder which ensures the proper parameters of the homogenisation and transport of the components of the composition.

The most widespread and the simplest method of producing polymer nanocomposites is the last of the presented techniques – intercalation in the melted state [6,8,9]. This method has been used in the Polymer Nanomaterial Processing Laboratory at the Chair of Chemistry and Technology of Polymers of the Cracow University of Technology to produce many nanocomposites of engineering polymers, including polypropylene and polyoxymethylene. The current works focus on improving the physical and chemical properties, including the mechanical strength and the barrier effect of the polyamide nanocomposites with montmorillonite.

2. Characteristics of raw materials

Polyamide-6 (PA-6) carrying the trade name of Tarnamid® T30 was purchased from Zakłady Azotowe w Tarnowie – Mościcach S.A.

Montmorillonite with the trade name of Dellite® 72T was supplied by Laviosa Chimica Mineraria S.p.A. This variety of montmorillonite is industrially modified with dimethylammonium salt containing two long hydrocarbon chains.

The absorbency was tested with the use of several fluids which are commonly used in the automotive sector, i.e.:

- demineralised water – purchased from FENIKS Sp. z o.o.;
- radiator fluid - PETRYGO Q - produced by Polski Koncern Naftowy ORLEN S.A.;
- washer fluid – purchased from FENIKS Sp. z o.o.;
- brake fluid – with the trade name: LOTOS DOT-4;
- gasoline – the BP 95 gasoline purchased at a BP gas station;
- 15% solution of road de-icing salt in demineralised water – the road de-icing salt supplied from Kopalnia Soli KŁODAWA S.A.

3. Characteristics of process machines, equipment and measurement apparatuses

The polymer nanocomposites were produced by means of a process mini-line (Fig. 1) which consists of the Rheomex PTW 16/25 XL concurrent twin-screw extruder manufactured by HAAKE Thermo Scientific, a cooling tub and the ZAMAK G-16/325 granulator. The materials were dried and conditioned in the Horyzont Spt 200 vacuum dryer, provided with the WT-6A vacuum pump achieving the maximum vacuum of 10 Pa. All materials used for tests in the form of beams were made by means of the ZAMAK WT 12 ZMK/102/09 laboratory piston injector.



Fig. 1. The pellets production line

4. Method of producing polyamide-6/montmorillonite nanocomposites

Before starting to produce nanocomposites, the raw materials were dried in the laboratory vacuum dryer. Polyamide was dried at the temperature of 80°C for 3 hours. Montmorillonite was dried at the temperature of 150°C, also for 3 hours. In both cases, the drying process took place in the vacuum of 0.8 kG/cm². After drying the raw materials, premixes of polyamide-6 with a 3% (m/m) addition of montmorillonite were made.

The nanocomposites were produced by the method of intercalation in a melt with the use of the process mini-line. For comparison, a pure polyamide matrix was also extruded.

The produced granulate was re-dried in the laboratory vacuum dryer at the temperature of 80°C for 2 hours and left in the vacuum of 0.8 kG/cm² until the moment when the granulate reached the room temperature level.

5. Test methods

The presented project involved measurements of the change of weight of the pure polyamide matrix samples and the polyamide nanocomposite samples with a 3% weight share of the industrially

modified montmorillonite. The samples were placed in vessels filled with 1 litre of a specific liquid used in the automotive sector and being soaked for nearly 164 days. Following this period, all samples underwent the flexural strength test and the obtained results were compared against the results of the reference samples.

6. Results and Discussion

The results of the tests performed (Fig. 2) clearly show that the samples soaked in demineralised water reached maximum absorbency after 84 days and the weight of the beams increased by 9.8% for polyamide-6 and by 9.7% for the nanocomposite. The results obtained for the samples soaked in the 15% (m/m) solution of de-icing road salt were close to the results presented for the pure demineralised water. However, that maximum value was reached not earlier than after 164 days of performing the tests. The maximum absorbency for the materials soaked in the radiator fluid was not reached. The diagrams show that there was a continuing increase tendency and the weight of the tested materials on day 164 was bigger by 7.5% for the beams with PA-6 and by 7.2% for the nanocomposite beams then their original weight.

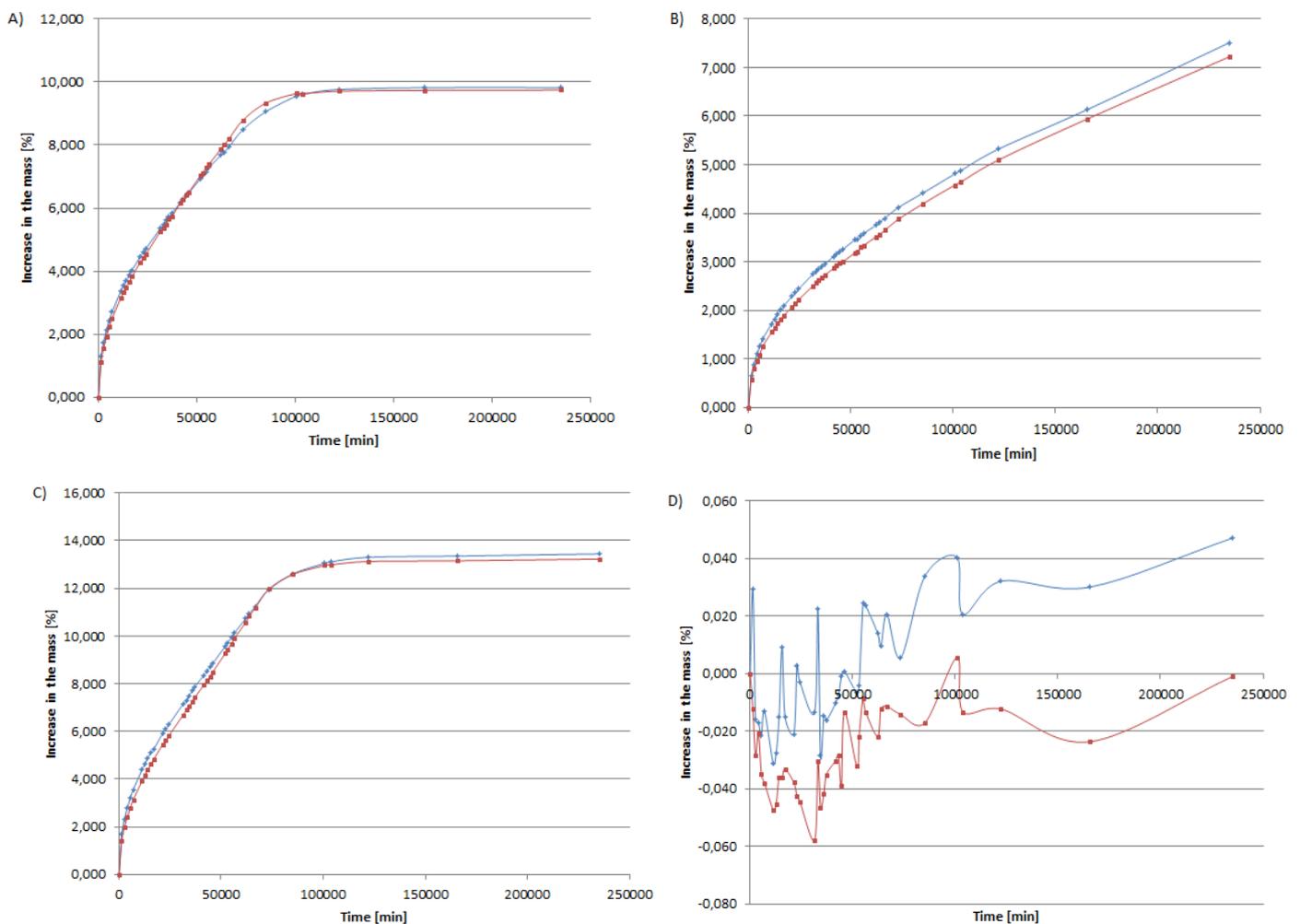


Fig. 2. The results of absorption: A) demineralized water, B) radiator fluid, C) washer fluid, D) brake fluid by PA-6 (blue line) and PA-6/MMT nanocomposite (red line)

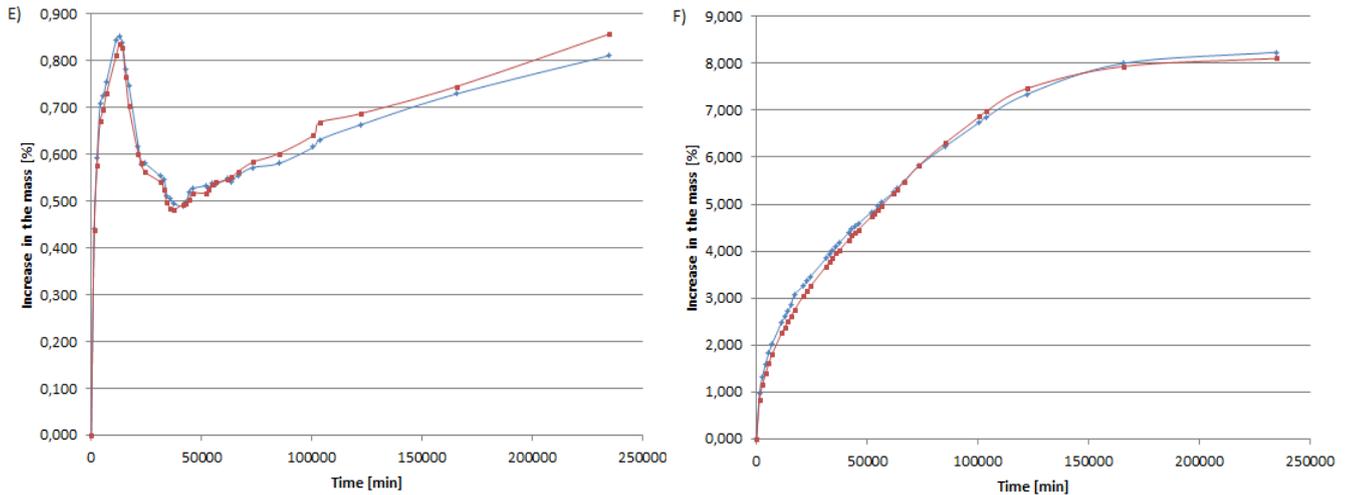


Fig. 2. The results of absorption: E) unleaded gasoline, F) 15 wt% salt solution road by PA-6 (blue line) and PA-6/MMT nanocomposite (red line)

The highest absorbency was reached for the winter washer fluid. In this case, the maximum values after 84 days were 13.3% for the pure matrix and 13.1% in case of the polyamide nanocomposite. Low absorbency was noticed in case of the samples soaked in gasoline. The maximum value reached during 164 days of performing the test equals 0.8%, both in case of PA-6 and PA-6/MMT. The most interesting result was obtained for the materials soaked in the brake fluid. The tested samples were not absorbing any fluid at all while their maximum absorbency values were only 0.047% after 164 days.

These results lead to the following conclusions. First of all, the absorbency of polyamide nanocomposite samples and the pure matrix remained virtually similar in all cases. Second of all, these materials are not suitable for producing applications where they will be in direct and long-lasting contact with polar solvents containing water or diethylene glycol. On the other hand, they are perfectly suitable for producing containers, fuel pumps and their components, e.g. connector, which will be in direct contact with propulsive fuel or brake fluid.

The supplementary information about the potential use of these materials was provided by the flexural strength test results. They confirmed the presumption that higher absorbency of fluids significantly reduces the mechanical strength of these materials. In the ranking presented on Fig. 3, the brake fluid turned out to be the winner. The mechanical properties of the materials soaked for 164 days in the brake fluid slightly increase rather than remain unchanged. This effect can be probably explained by the reaction between the molecules of compounds of which the fluid consists and the polyamide matrix. However, in order to acknowledge the rightness of these presumptions, it is necessary to repeat the mechanical tests and examine the structure of these materials both before the soaking and after 164 days. It can be stated here that the nanofiller addition increases the matrix strength only to a minimum degree and the mass production of the nanofiller is not of significance. However, it should be emphasised for the sceptics of nanotechnology that the tests were carried out for the 3% weight share. Considering the reports of the scientific literature, it can be expected that the increase of the weight share of the nanofiller will also cause an increase of the mechanical strength, giving green light for the implementation of these materials in the automotive sector.

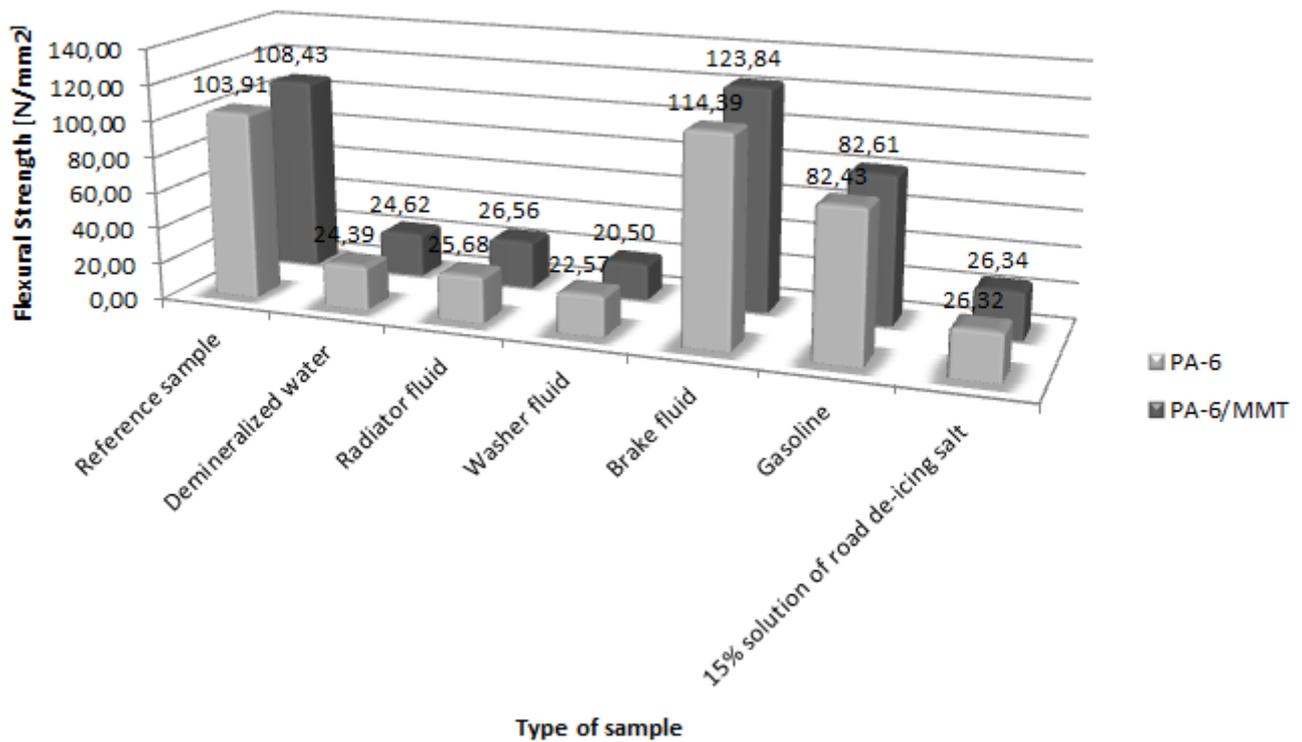


Fig. 3. The flexural strength of PA-6 and PA-6/MMT after 164 days immersion in automotive fluids

7. Conclusions

The analysis of the performed tests allowed for obtaining information regarding the maximum percentage absorbency of the particular tested fluids by PA-6/MMT nanocomposites and the PA-6 matrix. The time was recognized after which the given sample reaches the maximum absorbency and the continuation of soaking does not change the material weight any more. The flexural strength tests of the polyamide-6 and polyamide nanocomposite beams with montmorillonite, both before soaking as well as after 164 days of soaking in automotive fluids, proved the significance of the influence of the long-lasting contact of these materials with particular solutions on the mechanical properties. This provides the basic information about the use of these materials in automotive applications.

The presented results showed that products made of polyamide nanocomposites with montmorillonite can be used to produce fuel pumps and brake fluid reservoirs as well as fuel tanks. The materials produced are light and their mechanical strength is increased by adding nanofiller. Although the flexural strength values demonstrated by the nanocomposites are not surprisingly higher than the strength values of the matrix, it should be considered that, as far as the safety of people involved in a car accident is concerned, small values, and in this case the mechanical strength increase values, can frequently play an important part.

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