

INFLUENCE OF HNT NANO - ADDITIVES ON THE HARDNESS OF THERMOPLASTIC COMPOSITES

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Abstract

Nanocomposites are a new class of composites that are particle-filled composites in which at least one dimension of the dispersed particles is in the nanometer range. One of the interesting aspects of the use of nanofillers is the low concentration of that filler that needs to be added to the polymer system to obtain desired property improvements. Nanocomposites based on low-density polyethylene (LDPE), containing 2, 4 and 6wt% of Halloysite nanotubes (HNT) were used for experiments. The specimens were prepared by injection molding and were tested by Shore hardness test.

Key words: nanocomposite, injection molding, Low-Density Polyethylene, nanofillers, hardness

INTRODUCTION

Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. A nanometer is one-billionth of a meter; a sheet of paper is about 100,000 nanometers thick. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modelling, and manipulating matter at this length scale. At this level, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter. Nanotechnology research and development is directed towards understanding and creating

improved materials, devices, and systems that exploit these new properties [1-3].

Reinforcing thermoplastic polymers with nanotubes or nanoplatelets to form nanocomposites is a way to extend the usage of polymeric materials in engineering applications by improving their mechanical properties, namely elastic modulus and yield stress with filler contents as low as 5–10 wt% [1, 4, 5]. Furthermore, filler's shape, dimension, aspect ratio, and surface characteristics play a key role in determining the morphology, and thus, the thermo-mechanical, rheological, flame resistance, and optical properties of the final composite [6, 7].

Polymer Nanomaterials

Nanomaterials can be classified into nanostructured materials and nanophase/nanoparticle materials. The former usually refer to condensed bulk materials that are made of grains (agglomerates), with grain sizes in the nanometer size range, whereas the latter are usually the dispersive nanoparticles. The nanometer size covers a wide range, from 1 nm to as large as 100 to 200 nm. To distinguish nanomaterials from bulk, it is crucial to demonstrate the unique properties of nanomaterials and their prospective impacts in science and technology [8].

The development of these materials will enable the circumvention of classic material performance trade-offs by accessing new properties and exploiting unique synergies between materials, that only occur when the length scale of morphology and the fundamental physics associated with a property coincide, i.e., on the nanoscale level [9]. Multifunctional features attributable to polymer nanocomposites consist of improved thermal resistance and/or flame resistance, moisture resistance, decreased permeability, charge dissipation, and chemical resistance. Through control/alteration of the additives at the nanoscale level, one is able to maximize property enhancement of selected polymer systems to meet or exceed the requirements of current military, aerospace, and commercial applications. The technical approach involves the incorporation of nanoparticles into selected polymer matrix systems whereby nanoparticles may be surface-treated to provide hydrophobic characteristics and enhanced inclusion into the hydrophobic polymer matrix [9, 10].

The reinforcement of polymers using fillers, whether inorganic or organic, is common in modern plastics. Polymer nanocomposites, or the more inclusive term, polymer nanostructured

materials (PNMs), represent a radical alternative to these traditional filled polymers or polymer compositions. In contrast to traditional polymer systems where reinforcement is on the order of microns, polymer nanocomposites are exemplified by discrete constituents on the order of a few nanometers [1, 4, 5, 10].

EXPERIMENTAL PART

The aim of experimental part was to determine the effect of the added amount of HNT additives into LDPE material on the change of hardness that mechanical properties of thermoplastic composites.

The first step in preparing the LDPE composite is processing. Processing can be defined as the technology of converting raw polymer to materials in a desired shape. Polyethylene composites are processed by many techniques such as extrusion, injection molding, compression molding, and rotational molding. A large number of products are produced by injection molding [4, 7]. In injection molding process, the compounded specimens are preheated in cylindrical chamber to a temperature at which it can flow and then it is forced into a cold, closed mold cavity by means of quite high pressure, which is applied hydraulically through the ram or screw type plunger. The screw rotates to pick up the LDPE and melt it, mix the melt and deliver it to the closed mold. The screw is then moved forward to force a fixed volume of the molten polymer into the closed mold. After melting, LDPE is solidified in the cool mold, the screw rotates and moves backward to charge the polymer for the next cycle [11]. The specimens for testing were production by injection molding on injection molding machine type Arburg Allrounder 320 C 500 – 170 (Fig.1).



Fig. 1 Injection moulding machine type Arburg Allrounder 320 C

The injection process of the polymer compositions was performed under the following conditions:

- the temperature of the heating zones of the plasticizing system of the injection

moulding machine, starting with the hopper, equalled 100, 140, 160, 170 and 180 °C,

- the temperature in the feed opening zone was set at 30 °C,
- the total time of the injection process cycle equalled 34.16 second, including the cooling time of 20 second,
- injection pressure: 100 MPa,
- the holding pressure equalled 85 MPa,
- the temperature of the injection mould was set at 18 °C.

Material

The polymer used in the experimental tests was Low - Density Polyethylene (LDPE) marketed under the trade name Malen E and symbol FGAN 18-D003, produced by Basell Orlen Polyolefins Company. Some of the properties of the polyethylene, as specified by the manufacturer, are listed in Table 1. The recommended processing temperature for this product ranges from 170°C to 220°C.

The nano-additives used in the experiments were Halloysite nanotubes (HNT) in the form of powder of the grain diameter from 30 to 70 nm and length 1-3 µm, density 2530 kg/m³ specific and surface 64 m²/g. Halloysite is a naturally occurring member of the kaolin family of aluminosilicate clays. Halloysite can occur in several structures but predominantly exists as a tubular structure believed to be the result of hydrothermal alteration, or surface weathering of other aluminosilicate minerals [12, 13].

Polyethylene grafted with maleic anhydride (PE-*graft*-MA), by Sigma-Aldrich Company, as a compatibilizer was used. Its melt temperature was 105 °C and density 920 kg/m².

Table 1 Selected properties of the test polymer LDPE (producer data)

Property	Value
Density 23 °C, (kg/m ³)	921
Melt flow rate, (g/10 min)	0.28
Tensile strength at break, (MPa)	21
Tensile strain at break, (%)	360
Tensile modulus, (MPa)	220
Vicat softening temperature, (°C)	93
Shore D hardness 15s, (ShD)	50

Material for experiments was blended at the three volume concentrations of 2, 4 and 6 wt% of HNT within LDPE matrix and volume concentration of 5wt% of compatibility factor (PE-*graft*-MA) in LDPE polymer.

Labeling of specimens for testing is shown on Fig.2.

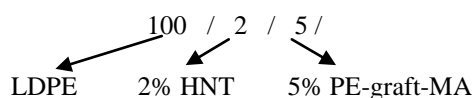


Fig. 2 Labeling of specimens for testing

Methods

Studies of selected mechanical properties of the moldings obtained with the change of HNT amount in LDPE matrix include measurements hardness Shore method (ShD).

Hardness is a mechanical property of the material, and it can be described as the resistance of the material to localized deformation. For polymer materials, several types of hardness tests that involve different shaped indenters are commonly used.

The testing was conducted according to the hardness measurement procedure described in the EN ISO 868:2005 standard. Plastics and ebonite – determining hardness using interference. Using a hardness testing machine (Shore method).

Hardness testing using Shore method was conducted in the following way: the specimen used for strength testing was placed on the measurement table and then to the surface of the specimen an indenter - D scale was applied. After a specified amount of time, the result of the hardness measurement was read. Five hardness measurements were made on each specimen and the final result is an arithmetic mean of these measurements.

Hardness tester Mitutoyo HardmaticHH-300 Shore D was used for experiments and is shown on Fig.3.

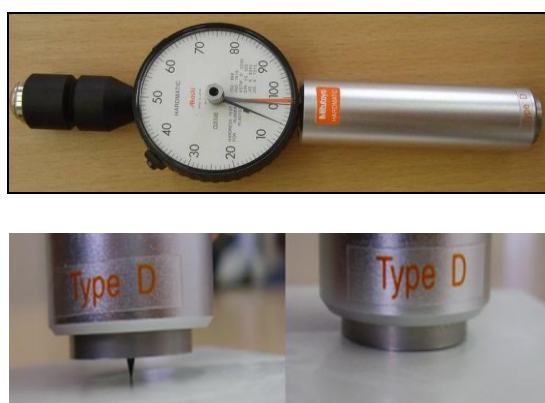


Fig. 3 Hardness tester Mitutoyo HardmaticHH-300 and indenter type Shore D

Results and discussion

Average hardness values of the tested materials are shown in Table 2 and graphically processed on the Figure 4.

Table 2 Shore’s hardness testing results of tested materials

Tested LDPE materials	Hardness Shore D [ShD]
100/0/0	51.3
100/2/0	50.7
100/4/0	50.0
100/6/0	51.2
100/2/5	50.7
100/4/5	49.8
100/6/5	50.1

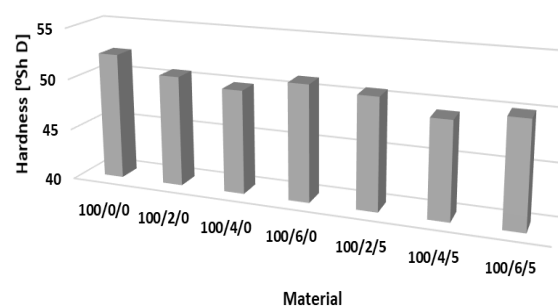


Fig. 4 The relationship between hardness and the mass content of the nanofiller with the addition (5%) of a compatibilizing agent

Figure 4 presents the relationship between Shore hardness and the mass content of the HNT in the matrix LDPE material. Based on these results it can be concluded that the highest Shore hardness value was measurement for the LDPE material (51.3 ShD). After addition of 2 to 6wt% nanofillers and 5% PE-graft-MA to the LDPE material, the hardness value was reduced. For example hardness value 49.8 ShD was measurement for the material LDPE with 4% HNT and 5% PE-graft-MA. Shore hardness at HNT content of 2wt% and 5% PE-graft-MA it is smaller by 1.16 % compared with the LDPE material, at HNT content of 4wt% and 5% PE-graft-MA is smaller by 2.9 % compared with the LDPE material and at HNT content of 6wt% and 5% PE-graft-MA is smaller by 2.3 % compared with the LDPE material. The hardness was decreased by adding the nanofiller and the compatibility factor PE-graft-MA into the LDPE material. The difference between the measured of the hardness values was minimal.

Conclusions

This study investigated the influence of Halloysite nanotubes (HNT) and PE-graft-MA within Low-Density Polyethylene (LDPE) matrix on the hardness. The hardness of specimens made by the injection molded were determined. The results of the tests conducted in this study on the effect of the mass content of the nanofiller (2, 4, 6wt %) with the addition (5%) of a compatibility agent demonstrated that the amount filler and compatibility factor PE-graft-MA has minimum effect on the hardness of the thermoplastic composites. Added of the nanofiller into LDPE material had no significant effect on hardness of tested materials.

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