POLYMERIC COMPOSITES BASED ON RIGID PVC AND ZINC OXIDE NANOPARTICLES

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The paper presents the processing and characterization of polymeric nanocomposites based on polyvinyl chloride plasticized with only 20% diisononyl phthalate for rigid and medical applications. In order to obtain materials with antibacterial and antifungal properties, functionalized zinc oxide nanoparticles were used. The functionalization was achieved with polydimethylsiloxane by ultrasonographic method in a control temperature environment. The influence of 1, 3, and 7 percent of functionalized zinc oxide nanoparticles were tested on the physical-mechanical properties, and the structure. The polymeric composites were processed on a Plasti-Corder Brabender 350 E mixer at 165-180°C and 150-180 revolutions per minute. The results show that adding zinc oxide nanoparticles into the composition led to an improvement in tear resistance, and tensile strength. Abrasion resistance present extremely good values. The FTIR spectra of the samples indicate that the new composites have a stable structure, due to a very good compatibility / interaction with the polymer matrix, the plasticizer does not tend to migrate to the surface.

Keywords: polyvinyl chloride, plasticizer, zinc oxide nanoparticles.

INTRODUCTION

The development of polymeric nanocomposites, structures with geometric dimensions below 100 nm, has a great influence on materials science due to their special properties (e.g. excellent mechanical properties, antimicrobial resistance, high temperature resistance and aggressive work environments). Therefore, new materials can be found in a wide variety of different applications, such as biomedical applications, consumer goods, health, medical or food technology, automobiles and transport (Vindizheva *et al.*, 2011; Vindizheva *et al.*, 2012).

Being one of the largest polymers, polyvinyl chloride (PVC) is widely used and essential in almost all fields. The optimal ratio of properties and costs makes PVC a material capable of competing with both natural materials and other polymers in many areas of science and engineering. The range of traditional materials for PVC compositions is wide. Polyvinyl polyvinyl chloride (PVC) is one of the most commonly used types of polymers (40% of dedicated polymeric materials) for biomedical and food applications. Medical grade and food grade PVC has been selected as a representative polymer for the matrix of antimicrobial composite systems.

There are different types of nanoparticles which can be incorporated in the polymeric matrix, selected according to their properties and their application. ZnO found various applications in plastic industry, medical packaging, cosmetics, medical devices (Saehana *et al.*, 2013), dentistry, and orthopedics, antibacterial coating (Arenas *et al.*, 2013), the textile industry (Bazant *et al.*, 2014; Alexandrescu *et al.*, 2017), etc. Antibacterial activity has been proven on various bacterial strains (Stegarus and Lengyel, 2017).

The paper present the obtaining process and characterization of polymeric composites based on rigid PVC. In order to obtain composites with antibacterial and antifungal properties, zinc oxide nanoparticles (ZnO) (Bazant *et al.*, 2014; Alexandrescu

et al., 2017) were used. To improve dispersion in the polymeric matrix of ZnO nanoparticles, they were functionalized (Mallakpour and Darvishzadeh, 2018a; Chung *et al.*, 2016; Mallakpour and Darvishzadeh, 2018b).

EXPERIMENTAL

Materials

Materials used to obtain the polymer composites based on plasticized polyvinyl chloride and ZnO nanoparticles are as follows: (1) PVC with a 70K-wert value, (2) Diisononyl phthalate (DINP) (density 0.98 g/cm³, boiling point 244 to 252°C, 99.5% purity, Mw= 418.618 g/mol), plasticizer, mainly used by the pharmaceutical, food and cosmetics industries, (3) PVC stabilizer - Calcium stearate (Ca content 11%, melting point 127°C), (4) Antioxidant Irganox 1010 (pentaerythritol tetrakis (3-(3,5 di-tert-butyl-4-hydroxyphenyl)propionate) from BASF Schweiz AG (active ingredient 98%, melting point of 40°C). (5) Functionalizing agent – polydimethylsiloxane –PDMS. (6) ZnO nanoparticles, white powder, with particle size of 21 nm from Sigma-Aldrich.

Method

The polymeric nanocomposites based on PVC matrix with ZnO functionalized nanoparticles was obtaining in several stages, as follow: functioning of nanoparticles, PVC plasticizing, obtaining, and test polymeric composites.

The functionalization stage of nanoparticles was achieved in an ultrasonic bath at 40°C with the functionalizing agent - polydimethylsiloxane (PDMS) added in drops over ZnO nanoparticles.

PVC plasticizing was achieved by absorption of plasticizer (DINP) into PVC by mixing them in a Plasticorder PLV 330 Brabender at 70 rpm, temperature 40°C for 10min. For a good thermal stability, temperature stabilizer and antioxidants were added.

Obtaining the polymer composites based on rigid PVC and functionalized ZnO nanoparticles on a Plasti-Corder Brabender Mixer 350 E, having the following features: 3 heating/cooling zones, range temperature 0-300°C, capacity 350 cm³, mixing speed 300 RPM max. Table 1 presents the formulations of rigid PVC/ZnO composites.

Processing technology: the temperature is set to 178°C, PVC containing stabilizer and antioxidant is added; after soaking and plasticizing (3 min.) the functionalized nanoparticles are added for 2 minutes. Continue mixing at a 150-180 revolutions per minute and temperature of 165°C for 3 minutes until the ingredients are embedded, and the mixture is homogeneous.

Table 1. Formulations of the polymer composites

Ingredients	Samples Codes			
	B1	B11	B12	B13
PVC – K 70 (g)	240	240	240	240
ZnO/PDMS (g)	-	2,4	7,2	12
Diisononyl phthalate (g)	60	60	60	60
Calcium stearate (g)	3	3	3	3
Irganox 1010 (g)	3	3	3	3

The specimen for physico-mechanical and structural characterization were obtained in an electrical laboratory press, by means of compression method, at a temperature of 175°C, preheating for 2 min, 5 min forming, and 5 min cooling both with a pressing force of 300 kN. Specimens of 150mm x 150mm x 2mm and 70mm x 70mm x 6mm, in a shape of a dumbbell, were obtained. Conditioned for 24 hours at room temperature, before being used for testing.

Figure 1. The overlapping Brabender mixing charts of control sample B1 and polymer composites based on 20% plasticized PVC with diisononylphthalate –DINP, and 1, 3, and 7% ZnO nanoparticles

The Brabender mixing charts (Figure 1) show that for samples with 20% diisononylphthalate plasticized PVC matrix, and embedding of 1, 3, and 7% ZnO nanoparticles, the maximum momentum times occurs at the same times, less than a minute, for the sample B11-B13. The forces increase to 200N/mm, as well as the temperatures, 265°C at the maximum torque and 165°C at the end of the process. This is due to the fact that the plasticizer used (diisononylphthalate) is more viscous, which implies higher forces, mixing times and temperatures.

Specimen Characterization

Physical-Mechanical Characteristics. Tensile strength and tearing strength tests were carried out with a Schopper strength tester with testing speed 460 mm/min, using dumb-bell shaped specimens according to ISO 37/2012, and angular test pieces (Type II) according to EN 12771/2003, respectively. Hardness was measured by using a hardness tester according to ISO 7619-1/2011 using 6-mm thick samples. Elasticity (rebound resilience) was evaluated with a Schob test machine using 6-mm thick samples, according to ISO 4662/2009.

The densities of elastomer samples were measured according to ISO 2781/2010.

Abrasion resistance was carried out according to ISO 4649/2010, the cylinder method, using a pressure of 10N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A wearing tester with abrasive cloth having granulation of 212–80 mm (PE 80). The samples used were obtained from rolled blends and pressed into sheets, then cutting with a rotating die and have cylindrical shape, with a diameter of 16mm and height of min. 6 mm.

Melt flow index was determinate at 180°C and a pressure force of 5 kg, with Melt Flow Index – Haake equipment.

Fourier transformed infrared spectroscopy (FT-IR). The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-530 cm^{-1} , using a 4200 FT-IR equipped with ATR crystal diamond and sapphire head.

RESULTS AND DISCUSSIONS

Physico-Mechanical and Rheological Characteristics

Table 2 shows the physico-mechanical and rheological characteristics of the polymeric composites obtained. The analysis of the results shows the following:

- The *hardness* of the control sample is 61°Sh A, and increases, with 2 units, up to 63°Sh A with the addition of nanoparticles, due to the nanofiller reinforcement effect;
- Constant elasticity, rigid values, are observed for this degree of plasticization, (20%) a performant feature of these materials;
- The *tensile strength* has a high value of 23 N/mm^2 and increases with the amount of nanofiller added into the compound;
- *Tear resistance* shows high values from 160 up to 177 N/mm , which present a rigid and performant material;
- The *elongation at break* shows small values, increasing from 240% up to 260% when adding 7% ZnO, this property increase proportionally to the amount of nanoparticles introduced into the composite. The values are small to the fact that this is a rigid PVC having only 20% plasticizer
- *Density* is 1.3 g/cm^3
- *Abrasion resistance* are extremely good, under 100 mm^3 , due to the small of amount of plasticizer and the effect of the nanoparticles, which made it more durable.

Table 2. Physical and mechanical characteristics for polymeric composites

Physico-mechanical tests	Samples Codes			
	B1	B11	B12	B13
Hardness, °Sh A	61	62	62	63
Elasticity, %	16	16	16	16
Tensile strength, N/mm^2	23,0	23,1	24,3	25,0
Elongation at break, %	260	240	260	260
Tear resistance, N/mm	160	167	172	177
Density, g/cm^3	1,3	1,3	1,3	1,3
Abrasion resistance, mm^3	97	97	102	108

Fourier Transform Infrared Spectroscopy (FT-IR)

The FTIR spectrum recorded on the simple PVC powder (Figure 2) shows numerous characteristic bands associated with this type of polymer.

Figure 3 show FTIR spectra of polymeric composites based on PVC plasticized with DINP containing ZnO nanoparticles functionalized with PDMS. Taking as a comparison the spectrum recorded on the simple PVC powder, it can be observed, for all spectra, the presence of functional groups derived from the plasticizer structure, namely the band characteristic of the carbonyl group (from about 1720 to 1121 cm^{-1} in the case of the mixture - B1) and those of 1724 and 1126 cm^{-1} for blends containing

ZnO / PDMS nanoparticles. The presence of carbonyl functional groups shows clearly that PVC plastification has been optimally achieved.

Figure 2. FTIR spectrum of PVC powder

Figure 3. FTIR spectra of composites based on plasticized PVC and ZnO nanoparticles: B1 - green, B11 - black, B12 - red, B13 - blue

There is a significant increase in the intensity of carbonyl groups at approximately 1724 cm^{-1} (Figure 3), which can be attributed to the fact that the plasticizer remains stable in the PVC structure (does not tend to migrate to the surface) due to a very good compatibility / interaction with the polymer matrix.

CONCLUSIONS

New types of polymeric composites based on polyvinyl chloride plasticized with 20% diisononyl phthalate containing zinc oxide nanoparticles were obtained. The functionalization of ZnO nanoparticles with polydimethylsiloxane was achieved by ultrasonic and constant temperature method. The PVC/ZnO nanocomposites were obtained on a Plasti-Corder Brabender Mixer 350 E at 178°C , 150–180 revolutions per minute and 165°C for 3 minutes, and a total processing time of 10 minutes. The temperatures at maximum momentum did exceed the scheduled temperature of 178°C .

going up to 260°C due to the fact that amount of plasticizer was only 20%. With the increase of the functionalized zinc oxide quantity, there was an increase in hardness, tear strength, and tear resistance, but low values for elongation at break. These properties were obtained due to the synergy of the functionalized ZnO nanoparticles and low plasticizer amount in the PVC matrix. The plasticizer does not tend to migrate to the surface, thus they can be easily processed by the injection method. New polymeric composites can be used in biomedical and food applications such as: blood bags and tubes, intravenous components, and containers, dialysis equipment, inhalation masks, examination gloves, packaging, footwear, etc.

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