POLYMERIC COMPOSITES BASED ON PLASTIFIED PVC AND ZINC OXIDE NANOPARTICLES

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The paper presents the obtaining method and characterization of polymeric composites based on polyvinyl chloride plasticized with 60% dipropylheptylphthalate for medical and food applications. In order to obtain materials with antibacterial and antifungal properties, specific to the mentioned domain, zinc oxide nanoparticles, functionalized with polydimethylsiloxane by ultrasonography, were used. The influence of 1, 3, and 7 parts of functionalized zinc oxide nanoparticles added to 100 parts of polymer, on the physical-mechanical properties, the melt flow index, the abrasion resistance and the structure, was investigated. The polymeric composites were processed on a Plasti-Corder Brabender 350 E mixer at 165-180°C and 150-180 revolutions per minute. The obtained show that adding zinc oxide nanoparticles into the composition led to an increase of hardness, max. 4°ShA, an improvement in tear resistance, elongation at break and resistance to tearing. Abrasion resistance has good values below 300 mm³. The melt flow index is over 62 g/10 min at 165°C with a 5 Kg pressure, showing very good processing by the injection method of the new polymeric composites. 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 although a large amount of plasticizer (60%) is used.

Keywords: polyvinyl chloride, nanofiller, zinc oxide.

INTRODUCTION

Poly (vinyl chloride) (PVC) is a versatile polymer, used in flexible, semirigid, and rigid forms. In worldwide plastic production, it is second only to polyolefin. The rapid expansion and consumption of PVC is due to lower cost, greater availability, good mechanical properties, and diversity of its properties (Titow, 1984; Braun and Bezdadea, 1986; Stelescu, 2013). It is the most used polymer in the manufacture of medical devices such as: blood bags and tubes, containers and intravenous components, dialysis equipment, inhalation masks and examination gloves, etc (Chiellini *et al.*, 2013).

The paper present the obtaining process and characterization of polymeric composites based on plasticized PVC for medical and food applications. In order to obtain composites with antibacterial and antifungal properties, specific for the medical/food domain, zinc oxide nanoparticles (ZnO) (Bazant *et al.*, 2014; Alexandrescu *et al.*, 2017) were used. The antibacterial activity of ZnO nanoparticles has been proven on various bacterial strains (Stegarus *et al.*, 2017). They even have antibacterial activity against spores resistant to high temperatures and high pressure (Elashmawi *et al.*, 2010; Arya *et al.*, 2016; Mallakpour and Darvishzadeh, 2018). To improve dispersion in the polymeric matrix of ZnO nanoparticles, they were functionalized (Mallakpour and Darvishzadeh, 2018; Chung *et al.*, 2016; Mallakpour and Darvishzadeh, 2018).

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) Dipropylheptylphthalate (DPHF) (density 0.984 g/cm³, pH 7, 99.5% purity), non-toxic 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) was produced by BASF Schweiz AG (active ingredient 98%, melting point of 40°C). (5) Functionalizing agent – polydimethylsiloxane -PDMS. (6) ZnO nanoparticles.

Polymer Composites Preparation

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

Functioning of ZnO nanoparticles was performed by ultrasonography with the functionalizing agent - polydimethylsiloxane (PDMS).

PVC plasticizing was achieved by absorption of plasticizer (DPHF) 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.

Preparing the polymer composites based on plasticized PVC and functionalized ZnO nanoparticles on a Plasti-Corder Brabender Mixer 350 E, with 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 plasticized PVC/ZnO composites. Processing technology: the temperature is set to 178°C, plasticized 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 is embedded, and the mixture is homogeneous. This operation was registered by the Plasti-Corder Brabender Mixer 350E recording system. The Brabender mixing charts (Figure 1) show that the maximum momentum occurs at 120-180s and the maximum mixing forces are small (18-20N/mm). Temperatures at the maximum momentum did not exceed the temperature of 178°C. This is due to the fact that a large amount of plasticizer (60%) has been used and mixing is slow (150-180 revolutions / minute).

Table 1. Formulations of the polymer composites

Ingredients	Samples Codes			
	C0	C1	C3	C7
PVC – K 70 (g)	100	100	100	100
ZnO/PDMS (g)	-	1	3	7
Dipropylheptylphthalate (g)	150	150	150	150
Calcium stearate (g)	2.5	2.5	2.5	2.5
Irganox 1010 (g)	2.5	2.5	2.5	2.5

The plates 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 (without pressing), 5 min modeling and 5 min cooling, both at a force of pressing of 300 kN. Specimens of 150mm x 150mm x 2mm and 70mm x 70mm x 6mm were obtained, and were conditioned for 24 hours at room temperature before being characterized.

Figure 1. Overlapped Brabender mixing charts: the control sample and polymer composites

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 47°Sh A, and increases with a few units up to 51°Sh A with the addition of nanoparticles, due to the nanofiller reinforcement effect;

- High elasticity values are observed for this degree of plasticization, (8-10%) a performant feature of these materials;
- *The tensile strength* is in the range of 3.7-5.8 N/mm² and increases with the amount of nanofiller introduced into the compound;
- *Tear resistance* shows high values (24-26.5 N/mm), which indicate a performant material;
- *The elongation at break* shows high values, increasing from 300% up to 500% when adding 7% ZnO, this property increase proportionally to the amount of nanoparticles introduced into the composite.
- *Density* is low, of 1.1 g/cm³ and the values for *abrasion resistance* are very good, under 300 mm³.
- The values for *melt flow* are higher due to the degree of plasticizer (60%) are between: 91 (control sample) and 62.3g/10 min. (165°C, 5 Kg force), indicating a very good processing by the injection method of the new polymeric composites. Values decrease when adding ZnO nanofiller as a result of reinforcement of the mixture.

Table 2. Physical and mechanical characteristics for polymeric composites

Physico-mechanical characteristics	Samples Codes			
	C0	C1	C3	C7
Hardness, °Sh A	47	51	51	51
Elasticity, %	8	10	10	10
Tensile strength, N /mm ²	3.7	5.0	5.3	5.8
Elongation at break, %	300	460	460	500
Tear resistance, N /mm	24	26.5	24	26.5
Density, g/cm ³	1.1	1.1	1.1	1.1
Abrasion resistance, mm ³	195	197	297	231
Melt flow index(165°C and 5 Kg force) g/10min	91.0	88.7	87.4	62.3

Fourier Transform Infrared Spectroscopy (FT-IR)

The FTIR spectrum recorded on the clean 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 DPHF containing ZnO nanoparticles functionalized with PDMS. For all composites, the presence of PVC characteristic groups can be observed. The appearance of additional bands (relative to the pure PVC spectrum) at approximately 1724 and 1121 cm⁻¹ is attributed to carbonyl (C = O) stretching vibration from the plasticizer structure - DPHF and confirms that plasticization of PVC has been successfully completed. The presence of the benzene ring in the DPHF at approximately 1429 cm⁻¹ could not be detected, in the obtained composites, since it overlaps the characteristic groups of PVC. However, at 739 cm⁻¹ (associated with the bending vibration, outside the plane), the presence of a benzene nucleus in the plasticizer can be emphasized, but at a much lower intensity. The presence of ZnO / PDMS nanoparticles could not be identified in the spectrum, because characteristic bands occur at approx. 526 cm⁻¹ which overlap also over the functional groups from the plasticizer structure. However, there is a significant increase in the intensity of the methylene groups at approximately 2923 and 2857 cm⁻¹ in the case of composites containing varying percentages of ZnO / PDMS (1, 3, and 7% respectively) relative to the control mixture, containing only plasticizer, due to the introduction of additional methylene groups derived from PDMS. The intensity of these

bands is the higher when increasing the amount of ZnO / PDMS introduced into the blend.

Figure 2. FTIR spectrum of PVC powder

Figure 3. FTIR spectra of composites based on plasticized PVC and ZnO nanoparticles: C0 - green line, C1 - brown line, C3 - red line, C7 - blue line

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 even at very high concentrations of plasticizer, it 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 60% dipropylheptyl phthalate containing zinc oxide nanoparticles functionalized with polydimethylsiloxane were obtained by ultrasonography. These 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 mixing time of 10 minutes. The temperatures at

maximum momentum did not exceed the scheduled temperature of 178°C due to the fact that a large amount of plasticizer (60%) was used and the mixing was slow. With the increase of the functionalized zinc oxide quantity, there was an increase in hardness, tear strength, elongation at break and tear resistance, and a decrease in the melt flow index. The new polymeric composites have a stable structure. 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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