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The influence of alkylammonium modified clays on the fungal resistance and biodeterioration of epoxy-clay nanocomposites

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ABSTRACT

In this work, the fungal resistance and fungistatic properties of epoxy-organo-montmorillonite nanocomposites have been studied in dependence on the type of alkylammonium-modified clay. The purpose of these investigations was the prediction of storage and operation timing under various conditions. The obtained polymer materials have demonstrated high fungal resistance in relation to the species of most aggressive microorganisms-biodestructors for polymers, as Aspergillus niger (Tiegh), Penicillium chrysogenum (Thom), and Trichoderma viridescens (A.S. Horne & H.S. Will.). However, no fungistatic effect of the clayes was found.

The analysis of the biodeterioraion degree of studied nanocomposites showed that the mold fungi species mentioned above result in the incidental deterioration of strength characteristics, and, in some cases, an improvement of physico–mechanical properties, which evidences high fungal resistance of the nanocomposites.

1. Introduction

Currently epoxy/layered silicate nanocomposites (ELSN) are widely used for various applications (Yen et al., 2001; Wang et al., 2005; Negi et al., 2009; Jung et al., 2012). It is explained by their particular phase morphology and interfacial properties due to highly dispersed silicate nanolayers in the polymer matrix. One of the most important problems of the ELSN use is their stability against destructive influence of microorganisms (biodeterioration) (Cappitelli et al., 2004; Sadat-Shojai and Ershad-Langroudi, 2009). The biodeterioration caused by the mold fungi, is one of the forms of the biological degradation of polymer materials. In recent decades, biodeterioration was particularly widespread, and it is the cause of colossal losses.

One of the most important factors determining the resistance of the ELSN to microbiological damage is their nature i.e. their chemical and physical structure Kumar et al. (2009). The rate and degree of microbiological damage of the polymeric materials based on ELSN depend considerably on the content of ELSN components such as: fillers, plasticizers, stabilizers, inhibitors, catalysts and other additives (Wagner et al., 1996; Roy et al., 2014). The biodeterioration leads to chemical destruction of the polymer chains and low-molecular additives of the polymer nanocomposites due to the products of mold fungi's metabolism, such as enzymes and organic acids Gnanavel et al. (2012). The ELSN biodeterioration results in decrease of its physico–chemical, mechanical, electric properties and performance characteristics. In addition, it would be worth noting that the mold fungi secrete in their metabolism process specific toxins, which provoke some human diseases (Johnson et al., 1993; Sabokbar et al., 2011; Irshad et al., 2013).

The degree of the ELSN damage provoked by microorganisms depends not only on the materials nature and type of microorganisms, but also on storage conditions and exploitation such as: temperature, humidity, light intensity, pH, and other factors. In any case, it is very important to use special fungicidal components, which fully (fungicidal effect) or partially (fungistatic effect) inhibit the activity of the mold fungi on the polymeric materials surface.

The problem of estimation of the polymeric material resistance to the biodegradation due to microorganisms action, as well as the search of ways to improve the stability of material are closely related to increasing the quality and reliability of products made with the use of such materials Goldman et al. (1998).

The estimation of the microbiological stability of the materials and choice of the most stable compositions are always associated

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with the study of their nature and with the degree of changes in their chemical and physical structure under microorganisms' influence. This last can formally characterize the possibility of complex polymer systems to conserve their inherent running ability and technological properties. Creation of the fungal-resistant polymeric materials based on thermosetting polymer matrices and organoclays is of great perspective, because both the elementary layers (plates) and the interlayer (basal) spacings in clays are of nanoscale range, what explains their highly developed active surface (Brown et al., 2000; Zhu and Njuguna, 2013). Therefore the used clays could be effective reservoirs for quaternary ammonium ions, which have fungicidal activity.

Moreover, further incorporation of nanofillers modified by cationic surfactants into the mentioned polymeric materials (Gorassi et al., 2003; Kozak and Domba, 2004; Xi et al., 2004) results in gradual diffusion of the fungicides toward the surface. This prolongs the fungal resistance of the polymer materials in time, i.e. will allow to obtain the material with the «long-term»activity.

Thus, an important problem of material science is to obtain new polymer materials with the fungal resistance. One of the ways to solve this problem is to create biologically stable nanocomposites based on synthetic polymers and montmorillonites (MMT) (Paul and Robeson, 2008).

The aim of this work was to study the obtaining of nanocomposites based on the epoxy resin and organo-modified montmorillonites with different types of alkylammonium clay modifier and to estimate the fungicidal resistance and the biodeterioration of the nanocomposites obtained.

2. Materials and methods

2.1. Materials

Epoxy resin used was liquid diglycidyl ether of bisphenol A (DGEBA) (Epoxy 520, Spolchemie, Czech) with epoxy equivalent weight 184. Diethylenetriamine (DETA, Dow Chemical), was used as a hardener. Four types of clay nanoparticles were used as fillers, three of them (Nanomer Na^+PGV, Nanomer I.28E and Nanomer I.30E) came from Nanocor Inc. and the other (Nanomer Na^+PGV(org)) was synthesized. Three types of clay nanoparticles were treated with an onium ion based on organic modifier or intercalant. Nanomer I.28E was modified with trimethyl stearyl ammonium (TMSA), Nanomer I.30E was modified with octadecyl ammonium (ODA) and Na^+Nanomer PGV(org) was modified with pentadecyl dimethyl benzyl ammonium (PDDMBA M_w = 0.3675 kg/mol). Inorganic sodium Na^+Nanomer PGV was unmodified with CEC = 145 $cmol_c/kg$ (dry basis).

Experimental procedure of the modification of Na^+Nanomer PGV(org) was carried out accordance to Calderon et al. (2008). Organo-modified clay was prepared by cationic exchange method, which is reaction between sodium cations of clay and both intercalation agents of PDDMBA.

1 g of Nanomer Na^+PGV was stirred in 500 mL of distilled water at the room temperature overnight. Then, 0.001 mmol/L PDDMBA was added to the stirring solution. After the addition, the exchange lasted for about 8 h. The organoclay was filtered and washed thoroughly with distilled water and then dried in an oven thoroughly.

2.2. Methods

SAXRD analysis was performed by using general-purpose X-ray diffractometer with graphite monochromator in the primary beam (CuKα radiation with $\lambda = 0.1542$ nm) with the scanning step of 0.02° and scanning range from 0.5° to 9° 2θ. The basal spacing of the clay was derived from the peak position (d_{001} reflection) in XRD patterns according to the Bragg equation ($\lambda = 2d\sin\theta$).

FTIR spectra were recorded using Spectrum One (Perkin Elmer) with KBr pellet method in the range of frequency 400–4000 cm−1.

The material has been examined to determine whether it remains inert or if it is nutritious substance for the growth of fungi according to the methods *A* and *B*. Intensity of the mold fungi growth has been evaluated according to ISO 846:1997 (International Standardization Organization, 1997).

To determine both the fungicidal resistance and fungistatic effect, the following groups of specimens were prepared: a) control specimens for comparative evaluation during the testing; b) specimens for testing under the influence of moisture; c) specimens for testing under the influence of the moisture and mold fungi. All the specimens were in tenfold replication. These latter were purified from external contaminants by dipping in ethanol for 1 min and then were dried. The test specimens were contaminated by isolates of the mold fungi: *Aspergillus niger* (Tiegh), *Penicillium chrysogenum* (Thom) and *Trichoderma viridescens* (A.S. Horne & H.S. Will.). The isolates were obtained from local populations of these species by soil cultivation and identified according to (Zerov, 1978; Index Fungorum database,). Used mold fungi are the most active biodecomposers for the polymers. The cultures were grown on a medium Czapek Dox Agar (HiMedia Laboratories Pvt. Ltd., India) in test tubes. Aqueous spore suspensions of the isolates were prepared at concentration of $1 \times 10^6 \pm 2$ spores/ml. The concentrations of spores in the suspensions were calculated using a Goryaev camera. The spore suspensions of each fungal isolate were mixed in equal proportions and then used to contaminate the test specimens.

Fungicidal resistance was estimated according to the method *A*. The specimens were placed separately in sterilized Petri dishes with a mineral salt medium (MSM) without carbon source. Then, they were sprayed by mixed spore suspension. MSM solution contained 2.0 g $NaNO_3$; 1 g K_2HPO_4; 0.5 g; $MgSO_4 \cdot 7H_2O$; 0.5 g KCl; 0.01 g $FeSO_4 \cdot 7H_2O$ per 1 L of distillated water. Final pH (at 25 °C) was 6 ± 0.2. The specimens were incubated at 24 ± 1 °C and at the relative humidity of >95% for four weeks. After two and four weeks, the surfaces of the specimens were examined by stereoscopic microscope Micromed-1 with photocamera of SciencaLab DCM 130 (at magnification of ×200).

Determination of the fungistatic effect was performed according to the method *B*. The test specimens were exposed with mixed suspension of the mold fungi spores in the sterilized complete Czapek Dox nutrient medium. After two and four weeks, the specimens were examined visually.

Studies of the both fungicidal resistance and fungistatic effect were carried out according to the existing guidelines (International Standardization Organization, 1997).

The impact resistance and flexural strength were determined according to the Dynstat method (Valasek and Chocholous, 2013; German Institute for Standardization, 1983). Computing of the experimental data was performed using dispersion analysis and the Student's test in the software package STATISTICA 6.0. The degree of the polymer materials biodeterioration was estimated using the biodeterioration coefficients, obtained according to Eq. (1):

$$K_\alpha = \alpha_1/\alpha\ 100\%;\ K_\sigma = \sigma_1/\sigma\ 100\%, \quad (1)$$

where K_α and K_σ are degrees of biodeterioration under impact resistance and flexural strength, respectively; α, σ and α_1, σ_1– values of impact resistance and flexural strength of specimens before and after exposure of mold fungi, respectively.