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Nanocomposites of poly(vinyl chloride) with carbon nanotubes (CNT)

Georg Broza [a], Kazimierz Piszczek [b], Karl Schulte [a], Tomasz Sterzynski [b,*]

[a] *Technische Universität Hamburg-Harburg, Germany*
[b] *Akademia Techniczno Rolnicza, Bydgoszcz, Poland*

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Abstract

The nanocomposites of PVC with multi-walled carbon nanotubes and single wall carbon nanotubes were prepared in THF solution, followed by film casting. The scanning electron microscopy allowed to confirm a homogeneous distribution of the CNT's in the PVC matrix. Depending on the CNT's concentration, changes of sorption in methylene chloride as well as of the characteristic temperature of PVC transformation, determined by means of the DSC measurements, were found. The electrical measurements indicated an increase of the conductivity with growing CNT's content in the PVC matrix.

Keywords: Carbon nanotubes; Poly(vinyl chloride); B. Electrical properties; D. Differential scanning calorimetry (DSC); D. Scanning electron microscopy (SEM)

1. Introduction

Among the huge number of publications describing the thermoplastic polymers nanocomposites, the composites of hard or plasticized poly(vinyl chloride) (PVC) with montmorylonite present a subject of a relative low number of papers [1–8]. Usually, the composites of PVC with montmorylonite were prepared by the addition of nanoadditives into the PVC solution in tetrahydrofuran (THF), followed by the solvent vaporization or by melt blending [1–5]. In the case of melt blending [1,2] an increase of mechanical properties and of thermal stability was noted. There was also assumed that clay can serve as a plasticizer for PVC. On the contrary, by solution blending [3] the enhancement of properties was related to the formation of a partially intercalated structure. Another procedure described [6–8] was an *in situ* polymerization of PVC in the presence of montmorylonite or with silica nanospheres. Especially, the addition of silica nanospheres [8] during the PVC suspension polymerization led to the modification of grain morphology.

Up to now any paper presenting the nanocomposites of PVC with the carbon nanotubes (CNT) was found in the literature. The interest in the creation of nanocomposites based on the PVC matrix may be explained by an essential role played by this polymer. Poly(vinyl chloride) presents today an object of a manifold of applications, where its considerable environmental and chemical resistance, as well excellent mechanical properties, which may be widely regulated by an addition of plasticizers, may be cited. Therefore, the physical modification of the properties of this polymer, and specially the creation of an electrical conductivity, as well as an improvement of defined mechanical properties, was the based idea of this work.

The molten state processing of PVC may be done if a required gelation degree is achieved [9–15]. This effect is widely related to the structural changes of PVC. The gelation effect of PVC is mainly explained by the transformation of the primary structure into a certain state, in which a highly organized structure of secondary crystals and a network-like morphology of gelatinated polymer may coexist.

The creation of PVC nanocomposites with CNT and the characterization of its specific properties was the aim of the presented paper. The future interest is related to possible application of these nanocomposites where a high environ-

* Corresponding author. Tel.: +48 52 37 49 054; fax.: +48 52 3749 005.
E-mail address: Tomasz.Sterzynski@put.poznan.pl (T. Sterzynski).

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mental resistance may be combined with specific electrical conductivity.

Depending on the structure of carbon nanotubes various properties were observed [16,17]. As well the geometry (L/D ratio) as the number of layers of graphene sheet seems to play a significant role by the creation of polymeric nanocomposites and its properties. This was the reason of an independent research on the single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT), as it was done in a manifold of papers [18] describing the CNT composites with another polymers.

2. Experimental

2.1. Material preparation

The poly(vinyl chloride) used was the suspension PVC S61 (by Anwil SA) with the *k* value 61. The single-walled carbon nanotubes (SWCNT) used in this study were ready supplied by CNI Technology Co., TX, USA, synthesized by the HIPCO method. The diameter of the SWCNT was about 10 nm with a length of few μm, and purity >95 wt%. The very thin multi-walled carbon nanotubes (MWCNT) introduced into the investigated composites were supplied by Nanocyl S.A., Belgium with average diameter of about 10 nm, length of 0.1–10 μm, and carbon purity >95 wt%.

2.2. Preparation of nanocomposites

The solution of PVC in tetrahydrofuran (THF) of the following composition was prepared: 98.30 phr of THF, 1.65 phr of PVC S61, and 0.05 phr of stabilizer MOK 17 (Acros). The solution was prepared in a dark laboratory bottle, by slowly mixing during 24 h at an ambient temperature.

The composites of the PVC with SWCNT contents of 0.1 wt% and 0.2 wt%, and with MWCNT, contents between 5 wt% and 20 wt%, were prepared in the form of thin films cast from PVC solution in THF.

The aim of a multi-step procedure used to prepare the PVC + CNT nanocomposites was to achieve the distribution of the CNT in nanocomposites as homogeneous as possible.

In the first step the CNTs were dispersed in the PVC solution using a combined procedure: quick mixing and ultrasonication at room temperature during 5 min, alternatively three times every procedure. The second step was the preparation of thin films cast from the PVC solution in THF on a glass surface with controlled horizontal position. During the third step, after vacuum drying the cast films of PVC with CNTs were compression molded at 175 °C.

3. Measurements

To characterize the PVC + CNT nanocomposites the following measurements were realized: SEM observation of the morphology, DSC, the determination of sorption and measurements of the electrical properties.

The morphology of the fractured surface of the samples was investigated using a field emission scanning electron microscope (SEM-FEG) model LEO 1530 (Leo Electron Microscopy Ltd., Zeiss, Oberhochem, Germany).

The determination of the structure transition by melting of the primary crystals and formation of secondary structure was performed by means of a differential scanning calorimeter (DSC) (SEICO Instruments, Japan). The standard procedure performed was: samples of about 15 mg were heated from +50 to +240 °C at a scan rate of 10 °C/min.

The sorption measurement of the PVC nanocomposites was performed as described in [19] with methylene chloride as absorbed solvent. The samples in a form of circles, with a diameter of 8 mm, were cut from cast films of PVC-CNT nanocomposites, and placed in the round glass cuvette filled with methylene chloride. The dimensional variation of the diameter was recorded by camera, with a registration interval of 5 s. The expansion of the samples diameter was analysed in a function of time.

Electrical surface conductivity of the PVC nanocomposites with MWCNT was performed according to the four-point van der Pauw method, using a Hioki 7005 source and a Keithly 139 system.

4. Results

4.1. SEM observation

Depending on the nanocomposites composition, domains of a high homogeneity of CNT distribution, as well as agglomerates were found. In Fig. 1 the SEM observation of the PVC nanocomposites with 0.2 wt% of SWCNT, and in Fig. 2 the PVC nanocomposites with 20 wt% of MWCNT are presented. In both cases a fairly homogeneous distribution of the CNT in the PVC matrix, as produced by solvent mixing, may be seen.

Characteristic for all observed samples is the creation of a kind of CNT junction-like connection between the carbon nanotubes, seen in a form of cross points. This effect may be responsible for the changes of certain composites properties, as it is shown below.

It should be stressed that the applied CNT distribution technique, e.g. the use of the low concentration PVC solution, followed by vaporization of the solvent, may be considered as a technique by which a homogeneous composite morphology could be achieved. Another very important point is that in our case, due to the melt mixing, the carbon nanotubes were probably damaged to a very low extend. This is evidently the consequence of relatively low stresses applied to the mixture of PVC solution with CNT during the homogenization of the nanocomposites.

4.2. Sorption

The run of the expansion curves (effect of *methylene chloride* absorption) as a function of time are presented in Fig. 3. We have performed this test for four different