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Photochemical and thermal behaviours of poly(vinyl alcohol)/graphite oxide composites

Halina Kaczmarek*, Andrzej Podgórski[1]

Faculty of Chemistry, Nicolaus Copernicus University, Gagarin 7, 87-100 Toruń, Poland

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Abstract

The properties of poly(vinyl alcohol)/graphite oxide (PVAL/GO) composites were investigated during UV irradiation using a mercury lamp ($\lambda = 254$ nm). The course of photochemical reactions was monitored by FTIR and UV–vis absorption spectroscopies as well as by estimation of insoluble gel amount formed during crosslinking. Changes in average molecular weights resulting from main chain scission in PVAL were measured by gel permeation chromatography. Composite microstructure was characterized by scanning electron microscopy and X-ray diffraction. The thermal behaviour of composites was determined by a thermogravimetric analysis. It was found that 0.1–5.0% GO addition to polymer bulk slightly hampers photooxidative degradation of PVAL. Thermal degradation in PVAL composites starts at somewhat lower temperatures in the presence of GO but this trend is changed in UV-irradiated samples.

Keywords: Poly(vinyl alcohol), PVAL; Polymer composites; Graphite oxide; UV irradiation; Thermal stability

1. Introduction

Composite materials are made from two or more components forming separated physical phases with different shapes and sizes. Usually, the modifying agent (e.g. glass or plant fibres, ground minerals, plasticizers, other macromolecular compounds) is dispersed in a polymeric matrix [1]. Composites having the domains with dimension from micro- to nanometers are especially attractive to material science and technology because such systems have new, unique physical and chemical properties, which are not available in traditional plastics. It was reported that proper combination of starting raw constituents leads to enhancement of mechanical properties, higher thermal stability, improved gas barrier properties and reduced flammability of composites [2,3].

However, the photochemical properties of polymeric composites are not well documented. It was reported in a few recent publications that photooxidation in polymer-based nanocomposites is faster than that in unfilled matrix, which is caused by reduction of the degradation induction time [4,5].

Poly(vinyl alcohol) (PVAL) is a water-soluble synthetic polymer with a high hydrophilicity, biocompatibility and non-toxicity. The capacity of PVAL for hydrogel formation in the presence of crosslinking agents or upon electron beam and γ-irradiation additionally widens its applications. PVAL is used as warp sizing, paper coating agents, adhesives, a carrier in drug delivery, and a component of biomedical and packaging material [6,7]. The interest in mixing of PVAL with inorganic fillers is rapidly growing. One of the popular modifiers is carbon, which can be used in various polymorphic forms, e.g. carbon black, nanotubes or graphite [8,9]. Graphite, characterized by a layered structure, was recently studied in matrix of polystyrene [2,10,11], polyacrylamide [12], poly (acrylic acid) [13], poly(vinyl acetate) [14], polypyrrole [15], and poly(vinyl alcohol) [16,17]. Usually, before the preparation of graphite-reinforced plastic, modification on the hydrophobic

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* Corresponding author.
E-mail address: halina@chem.uni.torun.pl (H. Kaczmarek).

[1] Present address: Faculty of Fine Arts, Nicolaus Copernicus University, Sienkiewicza 30/32, 87-100 Toruń, Poland.

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filler surface is needed, which can be done by oxidizing agent treatment (for example, concentrated oxygen acids) [18–21]. After this process, graphite oxide (GO) containing hydroxyl, carbonyl and ether functional groups at the surface is formed (Scheme 1). These functional groups facilitate the adsorption of polar molecules and hydrophilic polymers by graphite particles [22]. If macromolecules are able to diffuse into parallel sheets (when the distance between them is not bigger than few nanometers), we can expect to obtain nanocomposites [14–17].

No work on the study of graphite effect on PVAL photochemical stability was found in the literature. Thus, the aim of this work was to examine the behaviour of PVAL containing small amount of GO upon UV irradiation and, moreover, to check if the exposure to UV changes the thermal stability of composites studied. Investigations of the influence of electromagnetic radiation on polymers are connected not only with aging of plastic products during their outdoor application but also with the effect of UV irradiation in the case of sterilization of composite-based materials for medical, pharmaceutical and food industry applications. The polymer's physicochemical properties before and after UV irradiation were evaluated using FTIR, DSC–TGA, GPC and scanning electron microscopy (SEM or TEM).

2. Experimental details

2.1. Materials

Poly(vinyl alcohol) (PVAL, Sigma–Aldrich) was used as supplied. Deacetylation degree of polymer was 98–99% and weight-average molecular weight 85,000–146,000 g/mol. Graphite (Merck) bulk density was 20–30 g/100 cm^3.

2.2. Composite preparation

Graphite oxide was prepared by the Hummers method [13–17,20], in which graphite is oxidized by a mixture of fuming nitric acid and sulphuric acid.

PVAL composites with different GO amounts (from 0.1% to 5.0%) were prepared by mixing of component solutions. Filler immersed in water was sonicated for 1 h then, PVAL aqueous solution was added to the GO suspension. This mixture was immediately subjected to further ultrasonication for 60 min. Films of polymeric composites were obtained by casting of the mixed solution onto levelled glass plates and water evaporation. The thus-obtained samples were carefully dried in a vacuum oven. Films of the same thickness were chosen for comparison of quantitative changes during UV irradiation or heating.

2.3. Irradiation

The samples were UV irradiated at room temperature and in air atmosphere with a low-pressure mercury vapour lamp (TUV-30W, Philips, Holland) emitting mainly 254 nm radiation. Incident light intensity, measured by an IL 1400A Radiometer (International Light, USA) was 3.12 mW/cm^2. Times of irradiation were 1–10 h, which correspond to 115–1150 kJ/m^2 doses.

2.4. Analysis

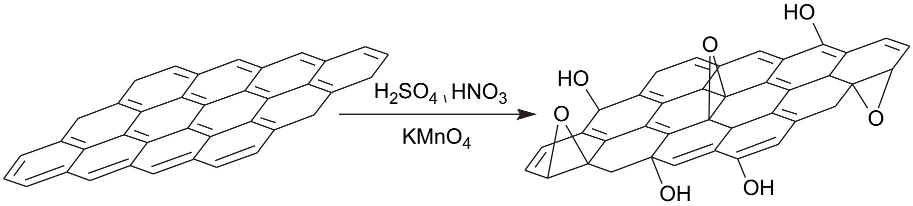
FTIR and UV–vis spectroscopies were performed using a Mattson Genesis II Spectrometer (USA) and a UV-1601PC Shimadzu Spectrometer (Japan), respectively. IR spectra were recorded as an average of 100 scans; the resolution was 2 cm^{-1}. The yield of photooxidative degradation was estimated on the basis of carbonyl and vinyl indexes calculated as a ratios of integral intensity of C=O or C=C bands to a CH$_2$ standard peak at 1420 cm^{-1}.

Gel permeation chromatography (GPC) was done using a Viscotek chromatograph (Texas, USA) equipped with two detectors – refractometric (Waters 410) and viscometric (Viscotek Model T50A) as well as two columns connected in line. The following parameters of measurement were applied: flow speed – 1 ml/min, temperature – 40.0 °C, concentration of polymer solution – 1.0 mg/ml, and sample volume – 100 µl. Deionized water was used as eluent. The column was calibrated with narrowly distributed pullulan standards SAC-10/7 Shodex.

X-ray diffraction (XRD) patterns were obtained using X-Pert PRO Systems (Philips) CuK radiation (α=154,056 Å) at a scanning rate of 0.02°/min in the 2θ ranges of 2–30°, voltage of 40 kV and a current of 30 mA.

Scanning electron microscopy (SEM) was carried out on a LEO-1430VP field-emitting scanning electron microscope at a low operating pressure and an accelerating voltage of 5.0–10.0 kV.

Transmission electron microscopy (TEM) was performed with a JEOL JEM 1100 model transmission electron microscope at 100 kV accelerating voltage.



Scheme 1. Surface oxidation of graphite.