

USE OF EXPANDED PERLITE AS GREEN FILLER FOR THE PREPARATION OF POLYVINYL CHLORIDE/PERLITE COMPOSITE

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The present study investigated using expanded perlite (EP), as an affordable and environmentally friendly filler for polyvinyl chloride. The oxidative chlorophosphorylation (OxyCh) reaction was used for preparing EP/PhPVC composite. To evaluate the effect of EP on the composite's mechanical, electrical, and physical characteristics, the PhPVC (without EP) have been obtained too. A comprehensive comparison methods were carried out on optical and electrical properties of PhPVC and, EP/PhPVC. Ultraviolet-visible spectrophotometric analysis (UV-vis) demonstrated the differences between measured optical bandgap energy (E_g) of both PhPVC and EP/PhPVC. It shows that owing to its enhanced adsorption capacity and better electro-optical properties, these materials are expected to find a suitable role in various practical applications.

Keywords: expanded perlite, polyvinylchloride, oxidative chlorophosphorylation, UV-analysis

INTRODUCTION

The design of materials, particularly polymer composites, urgently needs to be considered. The necessity to use already-existing industrial and ecologically friendly components in their production or through procedures like redesigning materials using straightforward and economical methods is what motivates this relevance. Many innovative polymer composites with appropriate qualities and efficient performance for the industrial and technological sectors have lately been developed based on these concepts [1].

Ever since its discovery in the early 19th century, polyvinyl chloride (PVC) has been a subject of ongoing research in the field of polymer science. Due to its direct manufacturing process (free radical polymerization), it has intrinsic structural faults that accentuate its unique characteristics, such as thermal stability. In addition to adding organic and inorganic thermal stabilizers, it has been suggested that better chemistry be used during PVC synthesis to lessen some of its inherent limiting characteristics [2]. Many years of continuous research have expanded our understanding of its chemistry, primarily through the chemical changes of this polymeric substance. Many chemical changes have been applied to the so-called anomalous or labile chlorine atoms, which are the tertiary and allylic chlorines as well as the usual secondary chlorines combined with a variable amount of carbon-carbon double bonds [3]. The latter were conducted not only for standard chemical reactions but also for improving the qualities, comprehending PVC-related phenomena, and applying PVC to particular uses. The many PVC reactions, which essentially entailed dechlorination, included

radical and nucleophilic substitutions, removal or dehydrochlorination, and grafting polymerizations through cationic and free radical routes [4]. Numerous modifications (plasticization, filling, and combination with other polymers [5-6]) are possible for polyvinyl chloride (PVC), and these options are ingrained in the material's chemical structure. Biomedical devices, membrane sensors, and ion-selective electrode membranes [7-8] were among the most popular and appealing uses of the chemically modified PVC with metals and functional groups.

Significant changes in the structure of PVC were noted as the concept of reinforcing additives (fillers) was applied to improve the properties of polymers, particularly when using another filler. Strong interfacial interaction of the filler with PVC resulted in improvements in optical and electrical properties [9]. Boundary layer development during PVC filling is linked to the polymer's chemical composition as well as changes in its supramolecular structure, mobility, packing density, and the emergence of orientational effects [10]. For example, some of the most common fillers for PVC are made from certain minerals, including some naturally occurring silicates (asbestos, talc, and clay) and naturally occurring (as well as synthetically produced) carbonates [11]. Employing the silicate minerals as a filler for PVC has been shown by Titov [12] is useful in some semi-transparent compositions because of its low tinctorial power and has particular interest in some electrical insulation applications. As the authors of the study have shown [13] the properties of carbonates, which make them desirable as fillers, include relative softness, good white color, purity, low plasticizer absorption, lack of water of crystallization, and generally good resistance to thermal decomposition during processing of the plastic compositions in which they are incorporated.

Gray to black in hue, perlite is an igneous rock that is created when volcanic eruptions cool [14-15]. SiO_2 , Al_2O_3 , K_2O , Na_2O , and mixed water make up the majority of its composition; but, depending on where it came from, it may also contain trace amounts of TiO_2 , CaO , MgO , and Fe_2O_3 . Water molecules evaporate from Perlite when it is heated to temperatures between 800 and 1100 °C. Consequently, the steam that is produced causes the perlite particles to expand, resulting in an approximate 20-fold increase in volume. Expanded perlite is a spherical filler that is directly used in the construction, agriculture, and environmental sectors [16].

There are relatively few investigations on the use of expanded perlite to produce polymer composites, despite its intriguing qualities including lightweight and low heat conductivity. Alosmanov et al. [17] reported that the addition of expanded perlite to butadiene rubber composite has a major effect on the thermal stability of the PhBR matrix, according to TG and DTG investigations of PhBR, EP/PhBR, and PhEP/PhBR made using the OxCh reaction. Furthermore, the effects of perlite addition on the PS matrix's morphological, mechanical, thermal, and rheological characteristics was examined by Amanda Gerhardt de Oliveira et al. [18]. The composites' morphology revealed that some parts of the perlite's spheres had been broken during processing. The analysis of thermal characteristics has been shown that the PS matrix's thermal stability remained unchanged upon the addition of perlite.

In the present work, industrial polymer– PVC was applied as a matrix for the preparation of EP/polymer composite using expanded perlite as affordable and environmentally friendly filler. The results of the research carried out may be useful in solving the problem of recycling PVC waste in order to create new materials with useful properties. In addition, most of the LDH/polymer nanocomposites have been combined with organic ceramics.

EXPERIMENTAL

Materials

PVC was purchased from the Sumgait Synthetic Rubber Plant (Baku, Azerbaijan). The EP was purchased from Bitlis (Turkey). Phosphorus trichloride (PCl_3), dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$), and sulfuric acid were used without further purification (Gorex Analyt GmbH, Bad Vilbel, Germany). Oxygen was supplied to the reaction medium by bubbling through the concentrated sulfuric acid.

Methods

Modification of industrial PVC by oxidative chlorophosphorylation reaction.

Phosphochlorinated PVC was prepared by oxidative chlorophosphorylation reaction followed by hydrolysis of the obtained modificate according to the procedure. For this purpose, 3.182 g of PVC was placed in a four-necked flat-bottomed flask to which 30 ml of dichloroethane was added and kept for two days for preliminary swelling in the solvent. Then the flask, previously equipped with a thermometer, a reflux condenser and a bubbler for oxygen supply, is placed on a magnetic stirrer and the polymer solution is heated under stirring to $\sim 70^\circ\text{C}$ until complete dissolution of the polymer has taken place. Then, after the polymer solution has cooled to room temperature, oxygen is introduced to solution at a rate of 7 l/h. After ~ 15 minutes, when the reaction medium is saturated with oxygen, the required amount of PCl_3 (3 ml + 2 ml) is added to the solution. The reaction is continued for 4 hours, after which the product obtained is subjected to hydrolysis. For this purpose, ice-cold deionized water is added to the flask and the hydrolysis is carried out at 50°C for 2 hours. Finally the product is separated from the solvent, washed several times with distilled water to neutral pH and then dried in the air. This product is named PhPVC.

Preparation of composite - phosphochlorinated PVC containing expanded perlite

Phosphochlorinated PVC containing expanded perlite was obtained by the following procedure. The 3,089 g of PVC placed in a four-necked flat-bottomed flask and 50 ml of dichloroethane was infused. The contents of the flask are left to swell in the solvent for two days. The polymer solution is then prepared by repeating the above procedures. Finally 0,3 g of expanded perlite was added to the prepared polymer solution and mix thoroughly. By repeating at least all the steps described above, a modified PVC containing perlite as filler is obtained. This product is named PhPVC/EP composite.

CHARACTERISATION

UV-Vis spectroscopy studies of the samples were carried out using the Specord 210 Plus UV-Vis spectrophotometer (Analytic Jena, Jena, Germany) in the wavelength range of 190–700 nm.

DISCUSSION AND CONCLUSIONS

Both PVC, PhPVC and its composite showed strong absorption in the UV region (fig.2). The EP/PhPVC and PhPVC showed considerably greater absorption compared to pure PVC at wavelength $\lambda = 280$ nm which can be assigned to the $\pi\text{-}\pi^*$ transition. The optical band gap of the EP, PVC, PhPVC and, EP/PhPVC composite was obtained using the approximate relationships among the reflectance (R), absorption coefficient (α), and scattering coefficient (s) based on Kubelka-Munk theory.

The band gap of the samples was obtained from the absorption coefficient (α) using the following equation [19]:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g)$$

The relationship for the parabolic bands at the beginning of the absorption edge served as the formula for this equation, in where x is an exponent that varies depending on the type of transition, A is a material constant, and $h\nu$ is the incident photon energy.

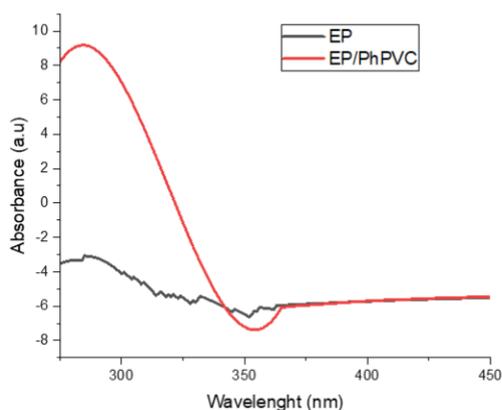


Figure 1. UV-vis spectra of expanded perlite, and EP/PhPVC polymer matrix

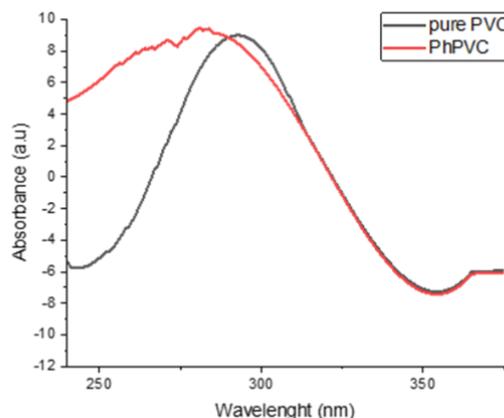


Figure 2. UV-vis spectra of pure PVC, and PhPVC

Band gap energy calculation of the EP, pure PVC, PhPVC, and EP/PhPVC is shown in fig. 3, respectively.

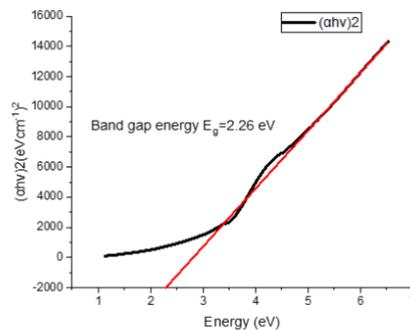
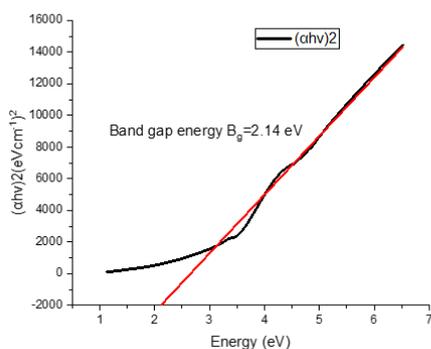
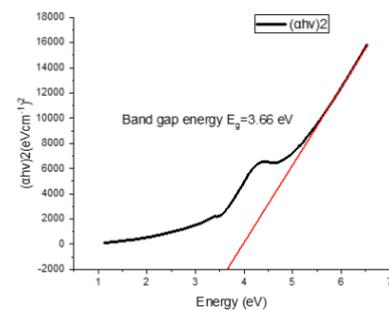
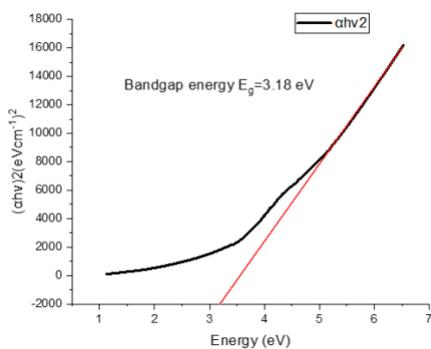


Figure 3. Band gap energy (E_g) of pure EP, pure PVC, PhPVC, and EP/PhPVC

The decrease in the direct and indirect band gap in the present case for the PhPVC and EP/PhPVC composite were attributed to the formation of polarons in the composite of the PVC loaded with EPs. Some modifications in the size of the amorphous domains in PVC due to the incorporation of EPs can also explain the optical band gap reduction for the polymer composite[20-21].

Our spectroscopic research demonstrates that the optical change in the EP/PhPVC composite and the induced electrical conductivity in the PhPVC are caused by radiation-induced dehydrochlorination of PVC.

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