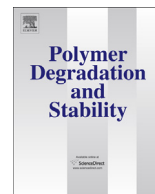




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## Polymer Degradation and Stability

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## Optimization of thermal and mechanical properties of bio-polymer based nanocomposites

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## ABSTRACT

This study aimed to improve the thermal properties of some biopolymers composites. Two aliphatic polyesters were used as matrix, the polylactic acid (PLA) and the polybutylene succinate (PBS). The filler used in the composites was expanded graphite (EG) with three different sizes, 5, 50 and 200  $\mu\text{m}$ . Thermal diffusivities were measured by infrared photothermal radiometry (PTR). Model of effective medium approximation (EMA) was used to study the effect on effective thermal conductivity  $k_e$  of thermal properties of matrix and fillers, the effect of the interfacial thermal resistance  $ITR$  between matrix and fillers or the effect of aspect ratio of fillers. Measurement of particles sizes of fillers before and after preparation process shows the presence of small particles, creating lower thermal conductivities than predicted by EMA model. Filtration of EG before process does not allow to increase  $k_e$  more than 6% because of mechanical stresses of the process. Finally silane functionalization is used to improve interactions between the fillers and the matrices in order to obtain better thermal conductivities. Mechanical studies on composites are also presented.

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### 1. Introduction

The polymer based nanocomposites have been used for several years in many industrial fields. They allow for an improvement of the pure polymer properties or they can create some properties that are almost non-existent in the neat materials such as gas permeability, fire resistance, electrical and thermal conductivity. This latter is particularly interesting as it offers new possibilities for replacing metal part in electric systems ([1,2]) or in flame retardant applications ([3], [4]). Additionally, industrial fields like automotive and aerospace are interested in thermally conductive polymer nanocomposites.

Different conductive particles as carbon nanotubes, graphene [5], metals [6], graphite [7], and expanded graphite [8–10] were used in literature. Expanded graphite (EG) caught our attention because of its special structure composed of stacked graphene nanosheets. It has about 50 nm thickness and has micrometric lateral size which allows a high aspect ratio including high

interaction surface with the polymer. This leads to an improvement of the thermal properties of polymers. Debelak et al. [8] worked on a EPON Resin/EG system and achieved 25 times the thermal conductivity of the neat polymer with  $\phi_{wt} = 20\%$  EG particles charge. This leaves no doubt about the effectiveness of the EG nanoparticles on improving the thermal properties of polymers. However, an analysis of literature shows that most polymers used originate from petrochemicals [1,8–11]. In recent years, the accumulation of toxic waste and the degradation of the ozone layer, among others, led to a gradual replacement of these polymers by those from renewable resources and/or biodegradable. Aliphatic polyesters represent an important family of biodegradable polymers. In this study, focus is on two polymers of this family: the polylactic acid (PLA) and the polybutylene succinate (PBS).

Silane derivatives (alkosylanes), good candidates to create functionalized groups at interface between polymer matrix and mineral charges, are used to improve the contact at the matrix/filler interface. Wu et al. [12] studied epoxy–functionalized carbon nanotubes (CNTs) composites with silane (3-Glycidoxypropyltrimethoxysilane, GPTMS) where they were actually able to show that the functionalization of the CNTs allow for a better dispersion of CNTs in the epoxy resin and also a better

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interaction at the polymer–fillers interfaces. This improvement of the adhesion at interfaces allowed for better thermal and mechanical properties. The technique was also used in 2008 by S. Ganguli [10] and epoxy/functionalized expanded graphite nanocomposites with silane treatment (3-aminopropoxyltriethoxysilane, APTS) were produced. A better stability of composites was highlighted and the thermal conductivity was increased by 33%. Wu et al. [13] recently worked on the subject and studied nanocomposites PMMA/functionalized expanded graphite with silane. They were interested in the fire-proofing character of the composite and were able to observe that the functionalized expanded graphite is a good candidate to improve the flame retardant capacity of the material. Other studies also were made by using other agents of coupling: Wang et al. [14] created isocyanate groupings on graphite by making reactions with some toluene-2,4-diisocyanate dipped into the dimethylsulfoxide. Tang et al. [15] was able to create covalent connections between the graphene and triazine. Ganguli [10] and T-C Wu [13] studied the reactions to the polymer–filler interfaces on epoxy resin and PMMA matrix respectively. From these studies, there is an emphasis of the improvement of the dispersion of the fillers of EG in a polymer matrix and the creation of connections in the interfaces of these two compounds. However, they do not report the influence of this functionalization on the thermal transfer of the studied polymers.

This paper focuses on the effect of the nanoparticles purity, the interfacial interactions between the matrices and the fillers, and the particle size distribution on the thermophysical properties of nanocomposites. Nanoparticles purity is achieved by purification, interfacial interactions and optimal particle size repartition are obtained by aminosilane functionalization and sieving respectively. Thermal properties were measured by photothermal radiometry technique and mechanical properties with a MTS Adamec Lhomargy-DY35XL tensile bench.

## 2. Materials and nanocomposites elaboration

The PLA and the PBS matrix are commercial extrusion grades respectively provided by Nature Works (PLA 4042D) and Nature Plast (PBE 003). All the PLA was plasticized with 15% of Triethylcitrate (TeC) provided by Sigma Aldrich. The plasticized PLA will be named PLA15. The expanded graphite was produced by EcophitG (Germany). It contains at least 95% carbon and has a density of 2.25g/cm<sup>3</sup>. In our study three different sizes of expanded graphite were used: 5, 50 and 200 μm. 3-aminopropoxyltrimethoxysilane (APTS) from Sigma Aldrich was used for the functionalization. The ethanol is also from the same company.

Nanocomposites were mainly prepared in a Haake thermo Fischer Rheomix 600 QC melt mixer at temperature of 175 °C and 145 °C for PLA15 and PBS respectively, for 10 min at 60 rpm. However, some samples are also prepared by extrusion in a mini twin screw extruder, Thermo Haake Minilab, in the same conditions in order to study the effect of preparation method on fillers repartition in polymer matrix. For thermal characterization, samples have circular shapes with a diameter of 1 cm and a thickness of about 0.5 mm. For mechanical characterization, according to ISO527-3, samples have a total length of 75 mm and a thickness of 3 mm.

The nanoparticles treatment is done in two steps, purification followed by functionalization. Purification reduces the impurities present in the expanded graphite and thus reduces outside influence contributing to the degradation of the polymer matrix. The expanded graphite is washed with ethanol deionizer water solvent (at a proportion of 85 and 15% respectively) until the residual solvent collected after the washing reaches a pH of 6 which

corresponds to that of the used solvent. It is reached after the second washing, thus indicating that the particles initially contained only a small amount of impurity.

In literature many processes can be found, but in this work, studies of [10] and [13] has been used to establish functionalization process. A first step of dispersion by ultrasonication during 2 h is followed by 5 h of magnetic stirring allowing silane grafting. 250 ml of solvent were used at 65 °C for 10 g of EG(5/50). The collected EG were washed and filtered until a pH of 6 is obtained. They are then dried in the open air for 12 h (to allow evaporation of the solvent) before drying in an oven at 65 °C for 6 h.

The different treatments studied are:

- 1) Pure particles (P).
- 2) Purified particles (PF): washing EG with demineralized water and filtration with solvent and water mixture (15/85 proportions) up to obtain a Ph of 6.
- 3) Purified particles + 15% wt. of APTS (FUNCT1).
- 4) Purified particles + 25% wt. of APTS (FUNCT2).
- 5) Purified particles + 35% wt. of APTS (FUNCT3).

## 3. Thermophysical and mechanical characterization

It is of interest to increase the thermal properties of composites to improve the heat dissipation in different systems without degrading mechanical properties. It is however necessary to distinguish steady state and transient phenomena [16]. Indeed, in steady states, the pertinent parameter is the thermal conductivity  $k$ , while thermal diffusivity  $a$  is important for transient phenomena like flame retardant applications. The relation between these two parameters is given by:  $a = k/(\rho C_p)$ . By using infrared photothermal radiometry (PTR), thermal diffusivity can be obtained. However, in order to compare experimental thermal diffusivity to effective thermal conductivity  $k_e$ , it is necessary to determine the volumetric heat capacity  $C = \rho C_p$ .

### 3.1. Static thermophysical parameters

During the sample preparation, the mass fraction of filler  $\phi_{wt}$  is used but models predicting the effective thermal conductivity use the volumetric fraction  $\phi_{vol}$  which can be obtained from  $\phi_{wt}$  with densities of fillers  $\rho_f$  and matrix  $\rho_m$ :

$$\phi_{vol} = \left[ 1 + \left( \phi_{wt}^{-1} - 1 \right) \left( \rho_f / \rho_m \right) \right]^{-1}$$

In the same way, the densities  $\rho$  and the mass specific heat capacity  $c_p$  can be calculated using linear rule of mixtures:

$$\rho = \phi_{vol} \rho_f + (1 - \phi_{vol}) \rho_m \text{ or } \rho^{-1} = \phi_{wt} \rho_f^{-1} + (1 - \phi_{wt}) \rho_m^{-1}$$

$$c_p = \phi_{wt} c_{pf} + (1 - \phi_{wt}) c_{pm}$$

Densities  $\rho$  and mass specific heat capacity  $c_p$  can be measured with a pycnometer and a DSC respectively but in this study, it is considered that for polymer/graphite composites the variations of  $\rho$  and  $c_p$  have opposite shapes and  $C$  is assume to be constant [11], [17].

### 3.2. Photothermal radiometry set-up

The method presented in Fig. 1, infrared photothermal radiometry (PTR), is a non contact and a non-destructive measurement technique. It allows for thermal diffusivity characterization of

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