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The Effect of HAP Modification on the Structure and Thermal Properties of Segmented Terpoly(ester-ether-ester)s (TEEEs)

Abstract

New organic/inorganic hybrid materials prepared from multiblock terpolymer as a polymeric matrix containing phthalic acid segments (PBT) as a hard block, hydrogenated dimer fatty acid (DLA) as a hydrophobic soft block and poly(ethylene glycol) (PEG) as a second soft block of a hydrophilic nature are presented in this work. Two types of nanocrystalline hydroxyapatites (non-calcined, HAP I, and sintered, HAP III) were used in an amount of 0.5 wt% as an inorganic phase within the hydrophilic/hydrophobic multiblock terpolymer matrix. DSC investigations revealed a two-phase structure of TEEE with a low-temperature glass transition ascribed to the amorphous phase of the soft segments (DLA and PEG) and a high-temperature melting point ascribed to the crystalline phase of PBT. The chemical structure and thermal properties of organic/inorganic composite (hybrid) materials were strongly dependent on the type of HAP: an increased glass transition temperature (T_g) and crystallization temperature (T_c) were found for composites containing sintered HAP III, while non-calcined HAP I had no influence on T_g and T_c as compared with the neat TEEE.

Key words: polyesters, crystallization, hydroxyapatite, composites.

Introduction

From the 1960s, an interest in thermoplastic elastomers (TPE) has been arising as a result of their good mechanical properties and the possibility of multiple, easy and economic processing [1, 2]. TPEs are materials of specific properties as a consequence of the lack of miscibility between the segments constituting the hard phase and soft phase. TPEs are an interesting group of materials with unique properties. Though macroscopically homogeneous, these polymers phase-separate at a microscopic (nanometer) scale. Thermoplastic elastomers are categorized as a new group of engineering polymers. Discreet plastic phases are embedded in the continuous elastomer phase and form *physical* crosslinks. Thermoplastic elastomers possess the properties of rubber-like materials (rubber-like elasticity) [3, 4], but they can be processed by traditional processing techniques as thermoplastics. Their processing can be carried out at temperatures higher than the glass temperature or melting point, which cre-

ates the possibility of multiple processing of thermoplastic elastomers [5]. By the selection of suitable monomers and their concentrations, various products of different hardness and elasticity, without the need to use additional plasticizers, can be prepared [4].

Many goods produced traditionally from rubber can be successfully produced from TPEs with regard to the simple processing and recycling of waste without a change in the material properties [3, 4]. This group of polymers has already found many applications in medicine including e.g. polymers for soft tissue reconstruction or drug delivery systems [4].

The development of new materials for the biomedical field requires different systems, such as polymer/ceramic composite materials, characterized by a combination of specific physico-chemical, mechanical, processing and biological properties. An interesting group of biodegradable and biocompatible polyesters

(PED) consists of materials containing oligo(butylene terephthalate) segments and sequences of dimer fatty acid (dilinoleic acid) [5]. Appropriately modified with poly(ethylene glycol) (PEG), they can form terpolymers of increased hydrophilicity and controlled degradation time [6, 7].

In this work, we report on the thermal properties and structure of multiblock PBT/DLA/PEG terpolymers (TEEEs) containing PEG of 1000 g/mol modified with two different nanocrystalline hydroxyapatites (HAP): non-calcined (HAP I) and sintered (HAP III). The materials were prepared in the presence of vitamin E (α -tocopherol, VE) as a thermal stabilizer.

Methods

The synthesis method of multiblock poly(ester-ether-ester) terpolymer was described in [8]. Nanocrystalline hydroxyapatite was incorporated into the polymer

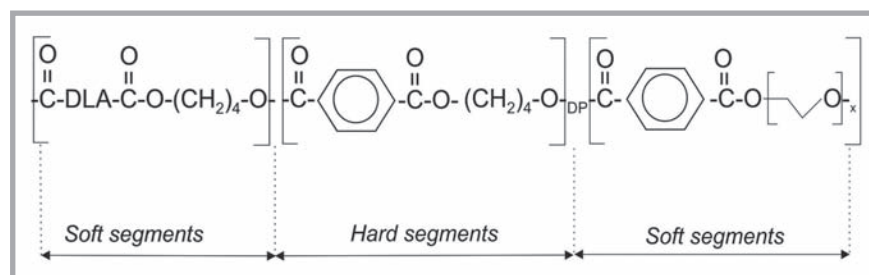


Figure 1. Structure of multiblock terpolymers (DP – degree of polycondensation of hard segments, $x=14$).

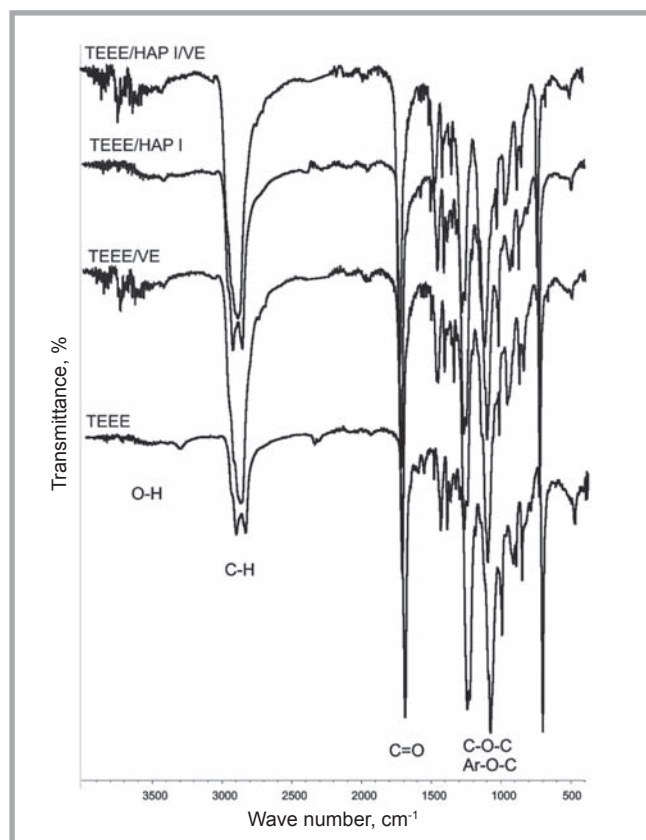


Figure 2. ATR-FTIR spectra of PBT/DLA/PEG₁₀₀₀ terpolymers with and without VE.

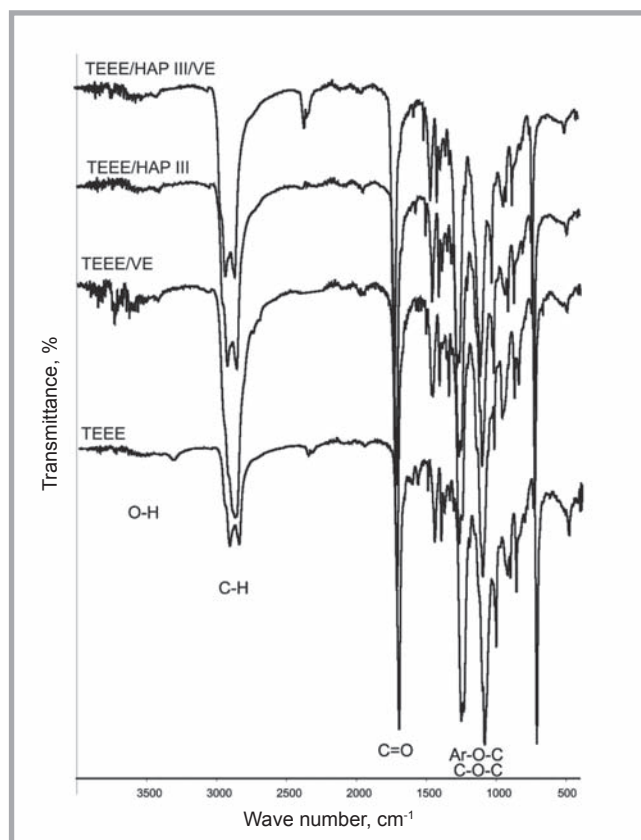


Figure 3. ATR-FTIR spectra of PBT/DLA/PEG₁₀₀₀ terpolymers with and without VE.

structure via the *in situ* polycondensation method, as described in [9].

Samples of the neat copolymer and hybrid materials were characterized by Fourier transform attenuated total reflection infrared spectroscopy (ATR-FTIR). Spectra were obtained using the Nexus FTIR spectrometer (Nicolet Instrument Corporation, U.S.A.) equipped with the Golden Gate Single Reflection Diamond

ATR (Specac INC, U.S.A.) scanning between 600 and 4000 cm⁻¹.

¹H NMR experiments were performed with a BRUKER AVANCE DPX spectrometer at 400 MHz. Chloroform was used as a solvent.

Differential scanning calorimetry (DSC) scans were performed with TA Instruments (DSC Q100) apparatus. The sam-

ples were dried in a vacuum at 70 °C and then kept in a desiccator. The process was carried out in a triple cycle: first heating, then cooling and a second heating in the temperature range from -120 °C to 30 °C higher than the melting point of each copolymer. The rate of heating and cooling was 10 °C min⁻¹. The glass transition temperature (T_g) was determined from the temperature diagrams as the midpoint on the curve inflection.

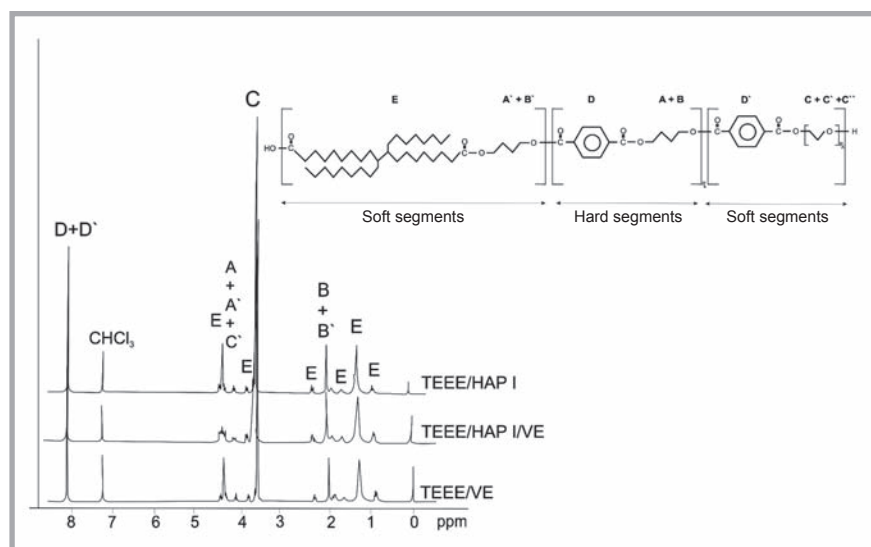


Figure 4. ¹H NMR spectrum of multiblock terpolymer modified with HAP I.

WAXS measurements were performed with diffraction apparatus TUR M62 equipped with a horizontal wide-angle goniometer HZG-4. The copper radiation CuK_α with a wavelength of 1.54 Å and monochromatization by nickel was used. The diffraction angle range 2θ was registered from 5° to 38° with a goniometer speed of 2°/min and at room temperature.

Results and discussion

The chemical structure of the neat multiblock PBT/DLA/PEG₁₀₀₀ terpolymer (**Figure 1**) containing 45 wt% hard segments (PBT), 19 wt% soft segments DLA and 36 wt% soft segments PEG₁₀₀₀ and its composites were studied using Fourier transform attenuated total reflec-

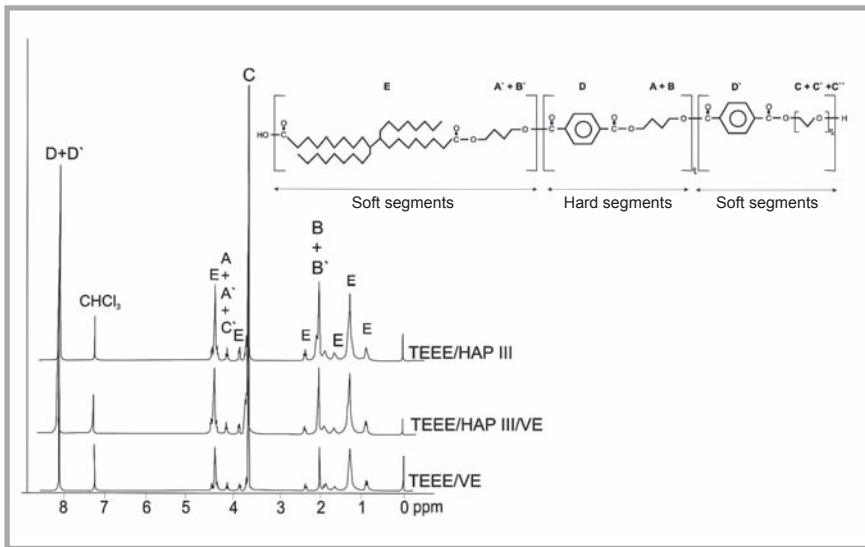


Figure 5. ^1H NMR spectrum of multiblock terpolymer modified with HAP III.

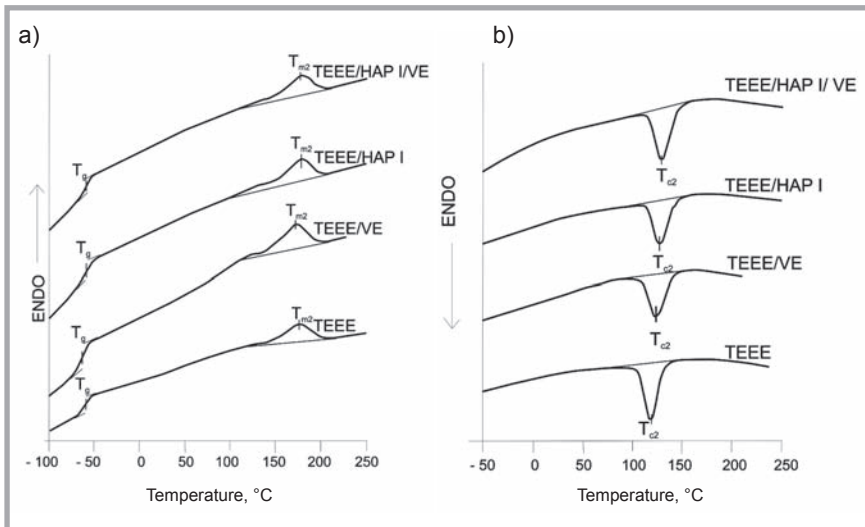


Figure 6. DSC thermogram during a) 2nd heating cycle and b) cooling multiblock terpolymers with HAP.

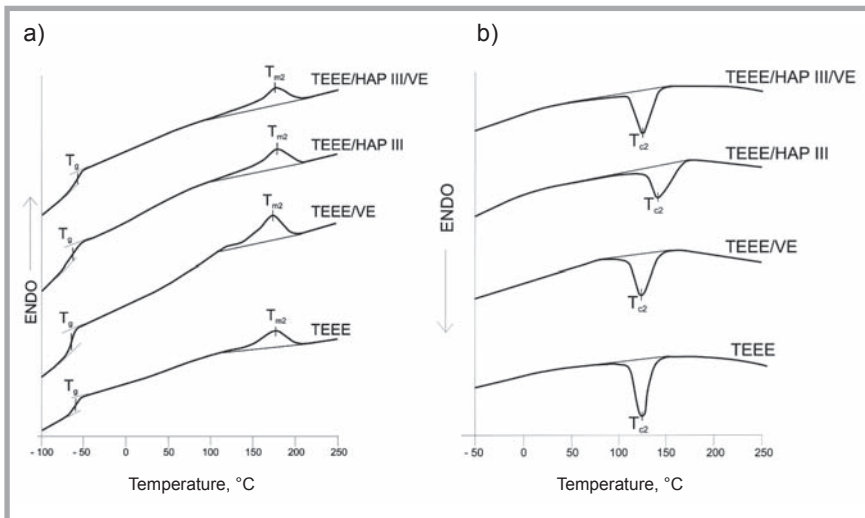


Figure 7. DSC thermogram during a) 2nd heating cycle and b) cooling multiblock terpolymers with HAP III.

tion infrared spectroscopy (ATR-FTIR). IR spectra for the neat multiblock PBT/DLA/PEG₁₀₀₀ terpolymer (Figures 2 and 3) revealed the presence of characteristic peaks confirming the expected chemical structure of the polymers. The peak at 1712 cm^{-1} was assigned to ν (C=O) stretching, characteristic of dimer acids. The bands at 2929 and 2856 cm^{-1} correspond to ν (C-H) stretching, and the high intensity reflected a high amount of aliphatic ester segments. A peak at 3500 cm^{-1} was attributed to the ν (O-H) end groups stretching. The bands at 1150 cm^{-1} corresponded to ν (C-O-C) stretching. This reflects the presence of ether segments of PEG₁₀₀₀. The ATR-FTIR spectra of the hybrid materials did not reveal any changes as compared with the neat multiblock terpolymer, indicating the lack of changes of the polymer chemical structure upon the addition of ceramic powder into the polymer matrix.

The polymer's composition was determined from the ^1H NMR spectra. The peak assignments of its structure are shown in Figures 4 and 5. The signals at 8.26 ppm represent the central methylene protons (from the hard and soft segments) and the two signals at 4.2 and 2.0 ppm characterize the terminal methylene protons from 1.4 – BD. The two signals at 4.5 and 3.87 ppm were ascribed to protons from PEG. Other signals represent protons from DLA.

The basic challenge with the use of HAP nanoparticles in TPE is the nanoreinforcement through the development of a “second” physical network. According to the main principle of the elastothermoplastic character of multiblock copolymers, at least one of the blocks has to be a soft (low T_g) material, such as a polyether in segmented poly(ether-ester)s or polyester in segmented poly(ester-amide)s. The second component must consist of a high T_g or T_m hard segment, and the hard and soft segments have to be chosen such that the free energy of mixing is positive [6]. Thus, the mutual incompatibility of the segments induces microphase separation in the solid state. A common tool to determine changes, such as phase segregation, glass transitions and melting, is a differential scanning calorimetry (DSC). The melting point (T_m), crystallization temperature (T_c) and glass transition temperature (T_g) were determined by DSC measurements and are shown in Figures 6 and 7. The addition of VE as compared with non-stabilized PBT/DLA/PEG₁₀₀₀

terpolymer increases the glass transition, T_g , and melting temperature, T_{m2} . The crystallization temperature, T_c , was not affected by the presence or absence of VE. The glass transition temperature, T_g , for systems containing HAPs and VE, added separately or together, showed, in general, increased T_g . Material containing HAP III (without VE) showed the lowest glass transition temperature of all the materials. The melting temperature, T_{m2} , was higher for materials containing HAP I and HAP III as compared with polymers without a ceramic filler. However, for hybrid systems (containing HAPs and VE), a lower melting point was observed as compared with materials containing HAPs only. The crystallization temperature, T_c , was found at 122 °C for terpolymer synthesized with the use of VE and without it. For material with HAP I, the crystallization temperature was higher than for material without HAP I. The sample with HAP III behaved differently. The PBT/DLA/PEG₁₀₀₀/HAP III sample showed T_c at 140 °C while the crystallization temperature for the hybrid materi-

al with HAP III and VE was comparable to the neat multiblock terpolymer.

In order to assess the polymer's structure, WAXS investigations were also performed. The diffractographs of multiblock terpolymer and hybrid materials are shown in **Figure 8** and they demonstrate the development of the crystalline phase. In general, two crystalline phases can be distinguished. The more pronounced reflections at 2Θ equal to 9.04° and 9.32° were observed for samples containing nanocrystalline HAP III (with and without VE). Other characteristic reflections were ascribed to the crystalline phase of PBT.

Conclusions

New terpoly(ester-ether-ester)s (TEEEs) were prepared in a two-stage process of transesterification and polycondensation from the melt in the presence of a thermal stabilizer (α -tocopherol, vitamin E, VE). New TEEE–nanometric hydroxyapatite (HAP I and HAP III) composites were prepared by *in situ* polymerization.

The IR and ¹H NMR results confirmed the chemical structure of the TEEEs. The DSC investigations showed the micro-separated two-phase structure of materials. The WAXS results confirmed the presence of a crystalline phase ascribed to the ceramic and PBT crystallites.

We demonstrated that the *in situ* polycondensation reaction from the melt can be considered as a very effective method of producing hybrid polymer/ceramic materials. The addition of nanoparticles increased the glass transition temperature of the hybrid systems as compared with the neat materials, showing T_g in a range from –58 °C to –62 °C, while the melting point, T_{m2} , was slightly increased (an increase from 176 °C to 178 °C as compared with 172.6 °C for PBT/DLA/PTMO₁₀₀₀ containing VE).

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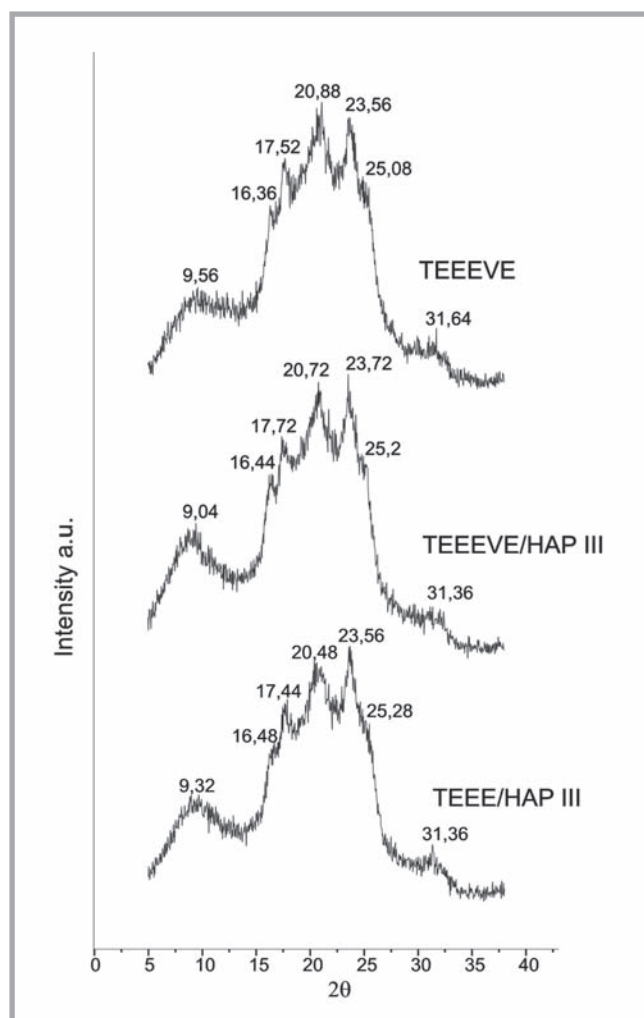


Figure 8. WAXS diffractographs of multiblock terpolymer with HAP III.

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