



Dielectric study of polystyrene/polycaprolactone composites prepared by miniemulsion polymerization



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ABSTRACT

Composite of polystyrene (PS) and a biodegradable polymer, polycaprolactone (PCL), has been prepared by miniemulsion polymerization technique. In the procedures, different amounts of commercial PCL were added during polymerization of PS in presence of sodium lauryl sulfate (SLS) as a surfactant. Formation of PS and PS/PCL nanoparticles was confirmed by Transmission Electron Microscope (TEM) and their structure was investigated using Fourier Transform Infra-Red (FTIR) and UV spectrometry. Encapsulation of PCL particles yielded nanoparticles of gradual enlargement in size as revealed by zeta sizer. However, significant information about the molecular dynamics within the composite and charge mobility can be realized by Broadband dielectric spectroscopy (BDS). So that, BDS has been employed to investigate the electrical and dielectric behavior of the considered composites over a wide range of frequency and temperature. It was found that the dielectric properties of the composites seem to be mainly due to the PS shell with no significant effect for presence of PCL in the core. The linear decrease of the real part of conductivity of the prepared blends with decreasing frequency just like the perfect insulator confirmed the encapsulation feature of the structure. The new materials can find applications in packaging, household beside biomedical fields.

1. Introduction

Polymer composites received much attention due to their versatile properties and applications. Preparation of the polymer composites can be carried out either by blending block technique or in situ formation of components. The advantage of the former method is that the used blending blocks have well-defined chemical structure and they do not undergo chemical change under processing conditions. Moreover, designed blending blocks and structure-property manipulation can be attained. On the other hand, the later technique for composite preparation is based upon the chemical transformation of at least one precursor during material preparation.

Polystyrene is a general-purpose synthetic polymer due to its hardness, clearness and low cost per unit weight. It finds many applications as protective packaging, containers and bottles. It is also characterized by its low gas barrier properties and low biodegradability. On the other hand, biodegradable polymers are characterized by their water resistance and being in the same time biodegradable [1,2]. Therefore, developed products can be obtained through compositing synthetic and biodegradable polymers in the fields of materials and packaging applications [3–6]. Blending of PS with PCL as a

biodegradable polymer has been thoroughly investigated by Biresaw et al. [7–9] Extensive study of the compatibility of the polymers in the blends using model biopolymers was performed. The study covered various properties such as interfacial tension, interfacial adhesion and tensile properties [10]. Mohamed et al. applied Fourier transform infrared photo-acoustic spectroscopy (FTIR-PAS) in order to confirm the presence of molecular interaction between PS and PCL in their blends [11]. Increasing dispersion of PCL and PS homo-polymers within one another in their blends could be achieved through addition of polystyrene–polycaprolactone diblock copolymer. The prepared blends showed improved flow and thermal characteristics in the range between the individual polymer components [12]. Miniemulsion polymerization is special type of emulsion polymerization technique in which a co-stabilizer is used and a shear is applied in order to obtain polymer particles in the range of 50–100 nm [13]. Another task for the co-stabilizer is to reduce the diffusional degradation rate of water/monomer emulsion along with reduction of monomer droplet size [14]. Synthesis of polystyrene of 50 nm particle size by miniemulsion technique has been reported. Reduction of interfacial tension and increase of colloidal stability of the nanoparticles of prepared PS can be attained by using higher levels of surfactants [15]. Zhang et al. described a

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method for preparation of polystyrene without co-stabilizer [16]. A fluorinated block copolymer prepared by ATRP and dodecafluoroheptyl methacrylate was used as the sole co-stabilizer in St miniemulsion instead of the conventional co-stabilizers. Better surface hydrophobicity was observed for the final latex. Encapsulation of nanoparticles in polymer matrix using miniemulsion polymerization technique was investigated extensively [14,17–19]. Polystyrene encapsulated nanosaponite composite suspension via miniemulsion polymerization has been reported [20]. Clay particle size and premodification of its surface were found to be crucial in order to produce stable latex suspension. Composite of silver nanoparticles encapsulated in polystyrene matrix been prepared [21,22]. The formed composite showed good antibacterial properties against *Escherichia coli* and *Staphylococcus aureus*.

The electrical and dielectric investigations of polymer composites attracted significant attention due to both basic and application fields. This is according to the fact that the prepared composite has its own characteristics, which is usually distinguishable from that of its individual components individual. Two factors play the main role in that context: the loaded ratio and the expected interaction between the components. Broadband dielectric spectroscopy (BDS) has become a powerful tool for investigations of the frequency and temperature dependence of different electrical and dielectric properties of the polymers and their composites [23–26]. Its broad range of frequency [10^{-6} - 10^{12}] is the main advantage over all other spectroscopy techniques since it covers all molecular dynamics, charge transportations as well as space charge or interfacial polarizations.

This work deals with encapsulated polycaprolactone, as a biodegradable polymer, in polystyrene latex as a novel way to prepare biocomposite of synthetic and biodegradable polymers. Characterization of the obtained nanocapsules has been performed and detailed study of electrical and dielectric properties of the synthesized composite has been demonstrated. In this context, the dielectric properties of the prepared composites will give valuable information about the structure and influence of polycaprolactone on the electrical and dielectric properties of the host polymer.

2. Experimental

2.1. Materials

Styrene, Sigma-Aldrich, was purified before being used. Polycaprolactone (PCL) Mwt = 80000 g/mol, ammonium peroxide sulfate (APS), sodium bicarbonate, hexadecane (HD), hydroquinone (HQ), and sodium lauryl sulfate (SLS) were obtained from Sigma-Aldrich and were used as received.

2.2. Methods

The mini-emulsion droplets were prepared by ultrasonication for 7 min (90% amplitude) with an ultrasonic disintegrator (Qsonic 450 W). Particle size distribution of the prepared PS and PS/PCL were measured by zeta sizer (Nano ZS, zeta sizer, Malvern, UK) based on the dynamic light scattering technique. The functional groups in the polymer composites backbones were identified and recorded using Perkin Elmer Fourier transform infrared spectroscopy (FTIR) with range of measurements of $600\text{--}4000\text{ cm}^{-1}$. Electronic absorption of the samples is investigated by UV absorbance measured by Jasco spectrometer V-630. Constant weights of the samples (10 mg/3 mL) were dissolved in THF and measured in quartz cuvette. The molecular weights of the prepared polystyrene and composites were determined using GPC Agilent model 1515 pump system equipped with 1260 infinity refractive index detector. THF was used as eluent operating with a flow rate of 1.00 mL/min and polystyrene was a standard. Investigation of structures of the prepared PS/PCL nanocomposites was carried out using transmission electron microscope (TEM). The samples were prepared by dropping a solution of the composite on a carbon-

coated copper grid (S160-3 Plano GmbH) and investigated using JEOL 200 TEM (Carl Zeiss NTS) operated at 120 kV/200 kV. Zero-loss energy filtering was used to increase the image contrast. Thermal gravimetric analysis was carried out using a Perkin Elmer thermogravimetric analyzer (TGA), with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere with flow rate 100 mL/min and temperature range from $30\text{ }^{\circ}\text{C}$ up to $600\text{ }^{\circ}\text{C}$. The dielectric measurements were performed between 0.1 Hz and 10 MHz using a Novocontrol high-resolution alpha analyzer. A Quatro temperature controller using pure nitrogen as heating agent and assuring temperature stability better than 0.2 K. assisted the analyzer. The investigated samples with thicknesses 1–2 mm were sandwiched between freshly polished brass electrodes with a top electrode diameter of 10 mm to form a parallel-plate capacitor cell. The complex permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) was measured using a sinusoidal voltage with amplitude 0.1 V over a 10^{-2} – 10^7 Hz frequency range in all experiments. Data were collected in isothermal frequency sweeps every $10\text{ }^{\circ}\text{C}$, from -50 to $120\text{ }^{\circ}\text{C}$.

2.3. Synthesis of composites

In round bottom flask, a specified amount of styrene monomer/PCL with different ratios (PCL 5, 10, 15 and 20 wt.%) and 0.037 mol of non-polar solvent (hexadecane, HD) were mixed and added to a solution containing 0.02 g sodium lauryl sulfate (SLS) in 73.28 g of water. The mixture was degassed (vac/ N_2 , followed by stirring for 20 min under N_2 at 300 min^{-1}) and then stirred for 50 min at 500 rpm. After that, miniemulsion droplets were prepared by ultra-sonication for 7 min. A slight stream of nitrogen was applied, and the emulsion was cooled with ice water. The formed mini-emulsion was transferred to the reaction vessel. After short degassing, the temperature was raised to $75\text{ }^{\circ}\text{C}$. Then, an aqueous solution of initiator was added (330 mg of APS in 7.1 g of water degassed under N_2 for 20 min). The reaction was performed at 600 rpm for 5 h. The reaction vessel was immersed in an ice bath to decrease the temperature until room temperature. The dispersion was precipitated in 300 mL of MeOH (1 wt% HQ), and the precipitation was done by dropwise addition. Polystyrene/polycaprolactone was filtrated and dried in a vacuum oven overnight.

3. Results and discussion

Preparation of PS/PCL composite has been carried out using mini-emulsion polymerization technique in order to increase miscibility and homogeneity of the newly formed composite. Different ratios of PCL (5–20% by weight) were added during polymerization of styrene. It is assumed that PCL particles are encapsulated within the PS during its formation (Scheme 1).

This assumption has been confirmed by TEM images (Fig. 1). Fig. 1-a, reveals that the prepared PS particles are in the range of 18–33 nm. On the other hand, addition of 15% PCL led to enlargement of the obtained particles by nearly 10 folds. These large particles confirm the encapsulation of PCL particles in form of a core and a PS shell is formed around them.

The particle mean size and distribution for the formed PS/PCL composite have been measured by zeta sizer. The results are depicted in Fig. 2, which show that the particle size of pure PS is in the range of 55 nm. By increasing added amount of PCL, the mean size and size distribution is not significantly modified for PCL content lower than 10%. Increasing the amount of PCL to 15–20 wt% leads to a significant increase in the mean size of the formed particles. However, no difference in the particle mean size and size distribution was evidenced by increasing the PCL content from 15 to 20%.

Molecular weight determination in the form of Mn, Mw and PDI of the pure PS and its composite with PCL, was carried out using GPC connected with a refractive index detector (RID). The values gathered in Table 1 showed that the highest molar mass was obtained for sample PS/PCL 20% while the lowest was for sample PS/PCL 10% which also

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