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Preparation and characterization of bio resin natural tannin/poly (vinylidene fluoride): A high dielectric performance nano-composite for electrical storage

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ABSTRACT

We have prepared films of polymer nano-composite (PNC) of poly [vinylidene-fluoride] (PVDF) and bio resin natural tannin (BRNT) nanoparticles. The α and γ electro-active phases were detected, and the addition of BRNT drastically increases the formation of the α-phase. Addition of BRNT produces up to 98% of electro-active phases. Robust electrostatic interactions arise between charges at the BRNT-surfaces, and differences in electron affinity between CH2 and CF2 groups created dielectric dipoles. The addition of BRNT has not only enhanced the formation of the electrically active phases but also makes each dipole in the phase has its specific characteristics for example its own relaxation time. The AC-electrical permittivity showed that the dielectric constant of 10%wt-BRNT nanoparticles in PVDF has a value 44 ε_0, which is four times more than the dielectric constant of the as-prepared PVDF films. These data show the importance of these polymers as easy, flexible, and durable energy storage materials.

1. Introduction

Lovinger [1] pioneered new polymer composites that are still attracting the interest of several researchers [2]. Kruusamäe et al. [3] have shown that electro-active polymers, in particular, have smart behaviors and different important applications: energy collection, biomaterials, sensors, actuators, etc. One of their interesting medical applications is their use as “artificial muscle” that behaves similar to real muscle. The material dilates when exposed to an external electric field, but shrinks when the electric field is removed. Thus, the electrical energy creates a mechanical force—this makes it a bio-transducer.

Poly-(vinylidene fluoride (PVDF) has an excellent combination of different properties in addition to its semi-crystalline nature. While producing more progress in the energy-harvesting area, electro-active polymers are promising materials for effective energy harvesting. The development of several scientific studies can produce high and efficient investments in renewable energy domains and in the ascendant polymeric energy harvesters' technologies.

This material is an important technology with a promising future in actuator and electric energy generation. In addition, some electro-active polymers have net piezo-, pyro- or ferro-electric properties such as the polyamide bio plastic Nylon-11 with superior thermal resistance [4]. Numerous electro-active polymers have shown different superior properties including poly(lactic acid) [5], poly-(lactic-co-glycolic) acid [6]. Concurrently, PVDF and its copolymers have excellent electro-active characteristics that vary depending on the internal structure. For example, by optimizing the geometry of PVDF chains and using quantum modeling calculations, Kepler [7] has demonstrated that different mean polarizabilities could be obtained depending on the vibrational-spectra that result from the interactions of the vibrational motions of the polymer chain. The mean value of the electrical dipole moment due to the monomer of the PVDF unit varies also from one electro-active phase to another: For both polymorphs the dipole moment per monomer unit converges to a nearly constant (5×10^{-3} °C m for alpha-PVDF and 8×10^{-3} °C m for beta-PVDF). Moreover, the magnitudes of the calculated dipole moment per monomer unit for a chain with 20 monomer units

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(5.2×10^{-3} °C m for alpha-PVDF and 8.3×10^{-3} °C.m for beta-PVDF) are different from the value calculated from C-F and C-H bonds (7.0×10^{-3} °C.m).[7]. Adhikary et al. [8] have reported that the dipole moment arises essentially due to the high difference between the electro-negativity of the fluorine atoms and other atoms such as carbon and hydrogen [8]. In these electro-active polymers, each chain has a dipole moment that is vertical to the chain itself. Due to different phases of PVDF, the beta phase has the highest dipole moment per unit cell (8×10^{-3} °C m [9]). The alpha and epsilon phases have no electrical activity because the packing of their dipole moment is anti parallel within the unit cell [10].

On the contrary, Rajesh et al. [11] have shown that the two active beta and gamma phases have a very high electro activity that makes them promising materials. These phases have serious applications in biomedicine [11], chemical warfare protection [12], batteries [13], sensors [14], actuators [15], magneto-electricity [16], filters [17], etc. Moreover, the gamma phase can store electric energy because of its strong dipole moments [18].

In addition, PVDF-nano-composites have received much recent attention due to their thermal, optical, electrical, dielectric, mechanical properties. versus other smart materials, electro-active polymers are relatively cheaper, pliable, and easier to prepare. Thus, due to the importance of electro-activity, numerous techniques have been developed to obtain these phases, and different scenarios have progressed to get new electro-active polymers. Huge interest has been given to reveal the dielectric properties of PVDF polymers in order to potential implementations in energy storage applications [19–22]. However, the dielectric losses are highly reduced due to the presence of some “conducting-fillers” that decrease the electrical breakdown. So, several authors have used nano-ceramics as substitution filler material as they produce low dielectric losses due to their poor conducting properties [23]. These nano-ceramics ameliorate the electrical energy density of the composite and its hardness.

BRNT has been chosen for two reasons: 1-Due to its narrow band gap (~2.3 eV-43% of the solar spectrum), BRNT has showed promised properties to be an excellent photo catalyst element which can be used for degradation of organics with promising applications notably in preserving the environment (obtaining clean water for example). 2- We were interested to examine the possibility whether addition of BRNT to nano-composite polymer films of PVDF would change the dielectric properties of these films. In fact, we found that BRNT improves the dielectric activity of the γ -phase in PVDF. This is due to the electrostatic interactions among the –CH2–/–CF2– dipoles of PVDF and the delocalized π-electrons. Also, the remaining oxygen functionalities of Fe-doped RGO via ion-dipole and/or hydrogen bonding interactions [24].

As a future work and in order to get some natural, new and efficient polymers, we think to link flavonoid tannins to PVDF (long carbohydrate chains) [24–28]. This would open the doors to some sorts of new natural-smart materials that have the ability to store high energy density.

In the present study, we selected natural tannin nanoparticles (BRNT-NPs) to be our filler material when preparation of PVDF nano-composite. BRNT-NPs stimulate the induction of electro-active phases (beta and gamma) in PVDF. Moreover, the dielectric properties of pure PVDF films have drastically improved upon addition of BRNT-NPs as filler. For example, the dielectric constant of pure PVDF is about $9\varepsilon_0$ at room temperature and 1 kHz; it increases markedly up to 44 ε_0 under the same conditions. This indicates that films of PVDF nano-composites are appropriate for energy storage across a vast range of frequency. For example, we have attained high values of energy density storage in PVDF nano-composites including 10.9 J cm^{-3} and losses of 4.9 J/cm^{-3}.

2. Experimental section

2.1. Materials

We used the following chemicals in order to prepare tannin: Mimosa (Acacia mearnsii, formerly mollissima de Wildt) bark tannin extract was provided by Silva Chimica (San Michele Mondovì, Italy). It contained 80%–82% actual flavonoid monomers and oligomers, 1% of amino and imino acids, the balance being composed mainly of oligomeric carbohydrates, mainly hemicellulose fragments, and some carbohydrate monomers. Raw mimosa bark extract, known as FINTAN OP on the market, was used in this work and was kindly supplied by the company SilvaTeam (San Michele Mondovi, Italy). The way it has been extracted from barks of Acacia Mearnsii (de Wild) and its composition have been detailed elsewhere [24]. Kolliphor© ELP, a commercial non-ionic solubiliser and emulsifier made by reacting castor oil with ethylene oxide in a molar ratio of 1:35, also known as Cremophor ELP or PEG-35 castor oil, and supplied by Sigma Aldrich, was used. However, other non-ionic surfactants, especially Tween 80, a polyethylene sorbitol ester commercialised by the same supplier, were also successfully tested. Hexamethylenetetramine (hexamine) was used as a cross-linking agent, and p-toluene sulphonic acid (pTSA) was used as a catalyst.

2.2. Synthesis

Emulsions were obtained by mechanical beating of an aqueous mixture of tannin, hexamine, pTSA and Kolliphor ELP, to which variable volumes of sun-flower oil were added. In a first step, 20 g of tannin were dissolved in 30 mL of distilled water, to which 0.7 g of pure pTSA was next added. The latter made the pH be equal to 3 for all formulations. The solution was stirred with a Teflon-lined blade mixer at 250 rpm over 20 min to ensure the homogeneity of the mixture. The surfactant was then added at a concentration of 1.4 wt% with respect to the total weight of aqueous solution, and stirring was continued over 20 min. In a second step, sun-flower oil was incorporated drop by drop, typically at a rate of 44 drops min 1, whereas the nascent emulsion was continuously stirred at 250 rpm. When half of the volume of oil was added, 4.47 g of hexamine (40 wt% in water) was poured in the emulsion. The mixing speed was briefly increased to 900 rpm for around 30 s, for an improved dissolution of hexamine, after which the mixing was adjusted again to 250 rpm. After all the oil fraction was added, the tannin-based emulsion was stirred for 10 additional minutes. This procedure allowed preparing stable emulsions containing volumes of oil within the range 30–160 mL. Considering the total volume of the emulsion, the oil fraction was thus roughly within the range 43–80 vol%. In other words, only part of these formulations corresponded to true HIPEs, however all emulsions behaved similarly. The resultant brown, homogeneous and very viscous emulsions were next covered with a protective film and cured at 85 °C for 20 h in a ventilated oven. After this time, which was found to be enough for a complete hardening, the monoliths were cooled down at room temperature, cut into smaller blocks for being installed in the cartridge of a Soxhlet extractor for 7 days during which oil was completely removed by refluxing acetone. After this time, the materials were let to dry in room conditions, leading to light brown, lightweight but strong, highly porous monoliths. These organic polyHIPEs were finally carbonised in a tubular horizontal furnace at 900 °C continuously flushed with high – purity nitrogen flowing of 100 mL/min. The heating rate and the dwell time were 3 °C/min 1 and 2 h, respectively. Next, the furnace was slowly cooled in nitrogen atmosphere down to room temperature. The resultant carboHIPEs fully retained their monolithic character.