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Effect of Plasticizers on Thermal Conductivity

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ABSTRACT: The effect of plasticizers on the thermal conductivity in different temperature regions has also been explained through the proposed formalism. $\lambda_j(\omega)$ and $S_j(\omega)$. Tg. and the change would be more if the additive forms cross-links as compared to the case when no cross linkage is formed.

Poly(propylene) (PP)/carbon black (CB) composites are melt-blended in a Brabender mixer with varying CB content. With the special-grade conductive CB, the surface resistivity of PP/CB composite was reduced by 13 orders of magnitudes by increasing the CB content from 0 to 15 wt%. The plasticizer poly(ethylene glycol) di-methyl ether (PEGDME) is used (0–5 wt%) to improve the dispersion of the CB in the polymer matrix and to reduce the surface resistivity of the composites. But the PEGDME plasticizer used here has no positive effect on the surface resistivity of the composites; in fact, it enhances the surface resistivity value by one order of magnitude at higher concentration (5 wt%). The scanning electron microscopy (SEM) pictures indicate that the presence of foreign material (plasticizer) especially at higher concentration disrupts the continuous carbon network inversely affecting the conductivity values. Finally, the optimization of the input variables (CB and PEGDME loading) is done using the design of experiment approach

KEYWORDS-plasticizers, thermal, conductivity, effect, cross linkage

I. INTRODUCTION

Biopolymers derived from sustainable sources such as plants, bacteria, and animal sources are in the center of attention of scientific research during the last years for environmental, sustainable, and biocompatibility reasons. Looking at the actual situation of plastic waste management, the biodegradability of biopolymers at the end of their life cycle presents great importance that situates biopolymers as a potential alternative to conventional plastics in many industries, especially plastics for short-term use [1]. The biocompatibility of many biopolymers also makes them very promising candidates for many biomedical applications, including wound healing, tissue engineering, drug delivery, medical devices, and scaffold fabrication [2,3].

Polyhydroxyalkanoates (PHAs) are linear polyester biopolymers produced by a wide variety of bacteria to store carbon and energy [4]. They are easy to extract using some organic solvents followed by precipitation in water. They are thermoplastics, i.e., they can be repeatedly softened by heating and hardened again on cooling and, in general, can be processed using the conventional processing equipment of plastics [5]. They are biocompatible and biodegradable biopolymers with many applications in the biomedical field as well as in the packaging industry [6,7,8].

PHAs can be produced as homopolymers or copolymers with different lengths of the side chain depending on the microorganism and the cultivation conditions. Poly(3-hydroxybutyrate) (PHB) is the most common PHA homopolymer that presents good mechanical and thermal properties as well as good processability. Despite that, PHB is known to be very brittle, which limits its application [7]. Copolymers of PHB with other hydroxyalkanoic acids with longer side chains show significant improvements in mechanical and thermal properties [9]. Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) is a medium-chain-length PHA copolymer that has been studied in the last years for different applications [10]. The hydroxyhexanoate fraction of the copolymer is known to decrease the polymer's crystallinity and the glass transition temperature, resulting in a more flexible polymer with a larger window of processing [11]. PHBH also showed better mechanical and processability properties than the widely studied small-



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chain PHA, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). It also showed better biocompatibility with a wide range of cell cultures than both PHB and PHBV [12,13,14,15].

Despite these promising data, the way of many biopolymers, including PHAs, into industry faces some difficulties such as high pricing compared to that of conventional plastics and metals; less availability of information about the structure-properties relationship; and the processing and mechanical limitations of some of them. Several ways are being followed to improve the mechanical and processability limitations of biopolymers in specific and polymers in general. Examples of these improvement approaches are chemical modifications, physical blending with other polymers, addition of fillers, and the use of plasticizers [5,16,17,18]. Plasticizers are materials with small molecular weight for promoting plasticity, flexibility, processability, and reducing brittleness [19]. Plasticizers enhance the processability by lowering the glass transition temperature (T_g), resulting in the reduction of the polymer's stiffness and brittleness, allowing polymer mixing and extrusion at lower temperatures, less pressure, and shorter time. The use of plasticizers also has more possible impacts on related physical properties of the plasticized polymer such as melting and crystallization temperatures, crystallinity, and permeability to water vapor and other gases [20].

Compared with other PHAs like PHB and PHBV, there is much less published research around PHBH. This paper investigates the fundamental structure-properties relationship of plasticized PHBH and aims to explore the effect of the usage of several molecules as plasticizers on the thermal, crystallinity, and gas permeability properties of PHBH films. These properties were studied analyzing the data obtained from TGA, DSC, XRD, and water vapor and oxygen transmission rates analysis. The effect of changing the plasticizer concentration on these properties was analyzed too. The PHBH films were prepared by film casting techniques. The parameters of the film casting, including the polymer solvent, the temperature of solvent evaporation, and the concentration of the polymer solution, were optimized to get smooth, homogeneous, and translucent films.[1,2,3]

Two novel plasticizers were selected in this study: isosorbide and glycerol diacetomolaurate (GDAL). Isosorbide is an innovative green biodegradable nontoxic plasticizer used recently for other biopolymers [21,22,23,24]. GDAL is also a nontoxic food-grade acetylated monoglyceride plasticizer that is reported as an effective plasticizer for PLA [20,25]. Poly(ethylene glycol) (PEG) with different molecular weights was also chosen as it is among the most investigated plasticizers, especially for biopolymers, besides being widely recognized as biocompatible materials [26]. Plasticized poly(vinyl chloride) (PVC) has been extensively utilized globally, with various applications in construction, piping, wiring and cable, installation, flooring, nonfood packing, windows, doors, and more. Phthalates have been the most commonly employed plasticizers for PVC, but some of these plasticizers demonstrate many toxic effects on the environment and human beings, which consequently limits the use of phthalate plasticizers. Growing awareness of the effects of plasticizers on the environment and the depletion of petroleum-based resources has made the development of an alternative biobased plasticizer for PVC formulation necessary. Recently, there has been an increased consciousness of the use of natural resource-based plasticizers instead of phthalates in PVC production, because they are eco-friendly in nature. This review paper covers the utilization of traditional and biobased plasticizers for PVC plasticization, and their effect on environmental, mechanical, and thermal properties has been reported.

II. DISCUSSION

In recent years, numerous research works have focused on the valorisation of biodegradable polymers obtained from organic waste. Materials derived from renewable sources containing polysaccharides, lipids and proteins can be consumed by microorganisms, especially by bacteria, in order to obtain monomers such as hydroxyalkanoic acids (with many structural variations) and d- and l-lactic acid [1]. These monomers have been used to produce polyhydroxyalkanoates (PHAs) and polylactic acid (PLA), respectively, two of the most important biodegradable polymers derived from renewable sources [2], [3].

PHAs are a family of linear polyesters of 3, 4, 5 and 6-hydroxyacids synthesised by a wide variety of bacteria, including strains of *Pseudomonas*, *Bacillus*, *Ralstonia*, *Aeromonas* or *Rhodobacter* [4]. These polymers are present in the cells as cytoplasmic inclusions, which are used as energy reserves [5], [6]. Depending on polymer composition, a



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wide range of PHAs with desirable properties can be obtained, from polymers which are stiff and crystalline to others that are flexible and rubbery [7].

Poly-hydroxybutyrate (PHB) is one the most widely studied PHAs [8], [9]. The physical properties of PHB are often compared to those of isotactic polypropylene because they have similar melting points, degrees of crystallinity and glass transition temperatures [10], [11]. PHB presents good processability, and it yields materials with a high degree of transparency and stiffness. Even if PHB has many interesting properties, its inherent brittleness, relatively low thermal stability, ageing behaviour and high cost of production restrict its range of applications [12], and thus it is often combined with other polymers such as PLA to obtain films with improved properties [13], [14], [15], [16].

PHB's great fragility is described as a result of different factors, which also contribute to its ageing behaviour: (1) secondary crystallization of the amorphous phase since its glass transition is close to room temperature; (2) low nucleation density, which leads to "large" spherulites or the appearance of cracks in the inter-spherulitic confinements that worsen the film's mechanical properties [17], [18]. In order to reduce the brittleness and thermal instability of PHB, copolymers like hydroxyvalerate (known as PHBV) have been obtained. As reported by Savenkova, Gercberga [19], these copolymers give rise to much less brittle materials, with higher extensibility, than the homopolymers; the higher the hydroxyvalerate content, the more flexible is the material.

Additionally, in order to reduce PHBV brittleness, different plasticizers have been used. These reduce the intermolecular forces along polymer chains, which improve the flexibility and chain mobility, at the same time that they provoke a decrease in glass transition temperature and changes in the crystallization behaviour. The effect of different kinds of plasticizers on the mechanical and thermal properties of PHBV matrices has been studied. Some of these are polyols, such as propylene glycol (PG) or glycerol (G), [20]; citrates, such as triethyl citrate (TEC) [21] and acetyl butyl citrate (ATBC) [12]; polyolefins, such as polyisobutylene [19]; dibutylphtalate (DBP) [21]; dibutyl sebacate [19]; oils and triglycerides, such as castor oil, soybean oil and epoxidised soybean oil (ESO) [20]; surfactants like sophorolipid [22] or poly-ethylene-glycol with medium molecular weight (PEG1000) [20]. In general, medium molecular weight substances with oxygen atoms (e.g. ethers or ketones), which are accessible for interactions with the polymer matrix, such as PEG1000, TEC or DBP, have effectively improved the films' stretchability [20]. The addition of some plasticizers hindered the PHB and PHBV crystallization in line with the interruption of interactions among the polymer chains [12], [17], [22]. However, some plasticizers, such as PG, PEG1000 or ESO, promoted molecular mobility, thus favouring the crystallization process [20].

PEGs of different molecular weight have already been used as effective plasticizers in different polymers [23], [24], [25], and could be a good alternative for PHBV matrices. No previous studies into the effect of the molecular weight of this compound on its plasticizing effectiveness in PHBV films have been found. Likewise, although surfactants, such as fatty acids, have been used as plasticizers in different matrices [26], [27], [28] their potential for PHBV plasticization has not been analysed either.

In this study, the effect of the addition of PEG with different molecular weight and two fatty acids (lauric acid or stearic acid) on crystallization behaviour and thermal stability, tensile properties and water affinity of PHBV films was characterized. In addition, the films were analysed in terms of their microstructural and optical properties, and the impact of storage under controlled conditions (ageing process) on film properties[4,5,6]

The effect of triethyl citrate (TEC) and different molecular weights and concentrations of polyethylene glycol (PEG), in addition to the effect of different water-soluble polymers and dispersions at different levels, hydroxypropyl methylcellulose (HPMC), methylcellulose (MC), carbomer 940, polyvinyl alcohol (PVA), ethyl cellulose (EC), on the mechanical and thermal properties, drug permeability, and porosity of free shellac films were investigated. Shellac films were cast from aqueous solutions, and their mechanical properties were studied by tensile test. Thermal analyses were performed using differential scanning calorimetry (DSC).



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The results showed that the addition of plasticizer caused a decrease in both elastic modulus and glass transition temperature (T_g) and an increase in elongation at break of free shellac films. This effect was related to the concentrations of plasticizers. Different molecular weights of PEGs have different plasticization mechanisms.

Moreover, the incorporation of different amounts of HPMC, MC, or carbomer in free shellac films caused an increase in the flexibility, decrease in T_g , and a marked increase in drug permeability of free shellac films, whereas the addition of PVA caused a decrease in flexibility and drug permeability and an increase in T_g . Addition of EC resulted in a slight decrease of the elasticity and a small decrease in drug permeability. However it does not show a considerable effect on the T_g . In addition, it was found that the drug permeability is directly related to the mechanical properties and T_g of shellac films.

III. RESULTS

A new plasticized nanocomposite polymer electrolyte based on poly (ethylene oxide) (PEO)-LiTf dispersed with ceramic filler (Al_2O_3) and plasticized with propylene carbonate (PC), ethylene carbonate (EC), and a mixture of EC and PC (EC+PC) have been studied for their ionic conductivity and thermal properties. The incorporation of plasticizers alone will yield polymer electrolytes with enhanced conductivity but with poor mechanical properties. However, mechanical properties can be improved by incorporating ceramic fillers to the plasticized system. Nanocomposite solid polymer electrolyte films (200–600 μm) were prepared by common solvent-casting method. In present work, we have shown the ionic conductivity can be substantially enhanced by using the combined effect of the plasticizers as well as the inert filler. It was revealed that the incorporating 15 wt.% Al_2O_3 filler in to PEO: LiTf polymer electrolyte significantly enhanced the ionic conductivity [$\sigma_{RT}(\max) = 7.8 \times 10^{-6} S cm^{-1}$]. It was interesting to observe that the addition of PC, EC, and mixture of EC and PC to the PEO: LiTf: 15 wt.% Al_2O_3 CPE showed further conductivity enhancement. The conductivity enhancement with EC is higher than PC. [7,8,9] However, mixture of plasticizer (EC+PC) showed maximum conductivity enhancement in the temperature range interest, giving the value [$\sigma_{RT}(\max) = 1.2 \times 10^{-4} S cm^{-1}$]. It is suggested that the addition of PC, EC, or a mixture of EC and PC leads to a lowering of glass transition temperature and increasing the amorphous phase of PEO and the fraction of PEO- Li^+ complex, corresponding to conductivity enhancement. Al_2O_3 filler would contribute to conductivity enhancement by transient hydrogen bonding of migrating ionic species with O–OH groups at the filler grain surface. The differential scanning calorimetry thermograms points towards the decrease of T_g , crystallite melting temperature, and melting enthalpy of PEO: LiTf: Al_2O_3 CPE after introducing plasticizers. The reduction of crystallinity and the increase in the amorphous phase content of the electrolyte, caused by the filler, also contributes to the observed conductivity enhancement.

Chitosan films were plasticized with four hydrophilic compounds, namely, glycerol (GLY), ethylene glycol (EG), poly(ethylene glycol) (PEG), and propylene glycol (PG). Our objective was to investigate the effect of plasticizers on mechanical and surface properties of chitosan films. The stability of plasticized films was observed by storage for 3 and 20 weeks in an environmental chamber at $50 \pm 5\%$ RH and $23 \pm 2^\circ C$. Plasticization improves the chitosan ductility, and typical stress–strain curves of plasticized films have the features of ductile materials, except the film made with 5% PG that exhibits as a brittle polymer and shows an antiplasticization effect. In most cases, the elongation of plasticized films decreases with the storage time, which might be due to the recrystallization of chitosan and the loss of moisture and plasticizer from the film matrix. Although at the beginning the mechanical properties of films made with PG, at high plasticizer concentration, are comparable to those of films made with EG, GLY, and PEG, their stability is poor and they tend to become brittle materials. The surface properties, analyzed by contact angle measurement, reveal that plasticization increases film hydrophilicity. It is found that GLY and PEG are more suitable as chitosan plasticizers than EG and PG by taking into account their plasticization efficiency and storage stability. Furthermore, a plasticizer concentration of 20% (w/w) with GLY or PEG seemingly is sufficient to obtain flexible chitosan film with a good stability for 5 months of storage.



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IV. CONCLUSION

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) films were prepared using a cast film technique. Dioxane was chosen over other polymer solvents as it resulted in homogenous films with better morphology. Several plasticizers with different molecular weights and concentrations were added to the biopolymer solution prior to casting. Thermal, crystalline, and permeability properties were analyzed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD), and both water vapor and oxygen transmission rate analysis. In general, the addition of plasticizers decreased the glass transition temperature (T_g), cold crystallization temperatures (T_{cc}), melting temperatures, as well as crystallinity degrees and increased the crystallite sizes and water vapor and oxygen transmission rates.[19,20] The use of isosorbide and low-molecular-weight poly(ethylene glycol) (PEG) lowered the T_g around 30 °C at the highest used concentration, also being the most effective in increasing the crystallite size. When considering isosorbide and low-molecular-weight poly(ethylene glycol) (PEG) as very good plasticizers for PHBH, the question of which plasticizer to use strongly relies on the desired PHBH application.[10,11,12]

A study examines the effects of varying the concentrations of sorbitol (S) and glycerol (G) on the physical, morphological, thermal, and mechanical properties of *Dioscorea hispida*, starch-based films. In this context, the films of *Dioscorea hispida* starch were developed using solution casting technique with glycerol (G), sorbitol (S), and a mixture of sorbitol-glycerol (SG) as plasticizers at the ratios of 0, 30, 45, and 60 wt%. [16,17,18]The films' moisture contents were increased when increasing the plasticizer contents. The tensile strengths were decreased, but elongations at break were increased; 7.38%–11.54% for G-plasticized films, 10.17%–15.76% for S-plasticized films, and 14.41%– 16.10% for SG-plasticized films with increasing plasticizer concentrations of the film samples. Varying plasticizer concentrations exhibited a minor effect on the S-plasticized film's thermal properties. Significant decrement in the glass transition temperatures of *Dioscorea hispida* starch films was observed when the plasticizer contents were raised from 30% to 60%. Significantly, the present work has shown that plasticized *Dioscorea hispida* starch can be considered a promising biopolymer for the applications of biodegradable films.[13,14,15]

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