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Chapter

POSS Fillers as a Factor Influencing on Viscoelastic Properties, Crystallization, and Thermo-Oxidative Degradation of Poly(Lactic Acid)-Epoxidized Natural Rubber PLA/ENR Blend

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Abstract

Polyhedral oligomeric silsesquioxanes (POSS) can be considered as the smallest silica particles that contain an inorganic cage-like silicon-oxygen structure surrounded by organic substituents. POSS are known to be reinforcing fillers able to enhance the fire retardancy and to increase the thermo-oxidative stability. The application of POSS with various functional groups and their effect on the properties of poly(lactic acid) (PLA) is analyzed based on the literature review. The influence of POSS with hydroxyl and glycidyl groups on the viscoelastic properties, crystallization, and thermo-oxidative degradation of PLA containing various contents of natural rubber ENR is discussed. The application of POSS with hydroxyl and glycidyl groups as an additive enhancing compatibility of PLA toughened by epoxidized rubber (ENR) is described. It is reported that POSS molecules with hydroxyl groups can enhance the thermo-oxidative stability of PLA melt.

Keywords: POSS, poly(lactic acid), epoxidized natural rubber ENR, viscoelastic properties, thermo-oxidative stability

1. Introduction

Nowadays polyhedral oligomeric silsesquioxanes (POSS) particles has received growing attentions as a new type of nanofillers used to prepare nanocomposites with enhanced thermal or mechanical properties [1, 2].

POSS has hybrid organic-inorganic structure, and it can be considered as the smallest functionalized silica particle containing a cage-like silicon-oxygen inorganic core surrounded by organic groups. Typical POSS structure has the formula $(RSiO_{1.5})_n$, where n = 6, 8, 10, and R are organic substituents at the corners of the inorganic cage [3]. The most common POSS structure has n = 8. Many research reports have been devoted to the various aspects of the application of POSS.

The inorganic core of POSS may provide molecular reinforcement, while the organic functional groups may increase the compatibility with polymeric matrix or be incorporated into polymeric network via co- and polymerization reactions [4].

POSS nanoparticles due to their flexible chemical and physical hybrid properties can be applied as functional additives able to reinforce, to toughen, and to stabilize various polymeric matrices, among them are polypropylene [5], polystyrene [6], polyamide [7], polyurethanes [8], and polysiloxane elastomer [9]. Herein the incorporation of POSS particles, which provide remarkable reinforcement at low filler loading, is advantageous and beneficial. Additionally POSS can be grafted to the polymer chains via chemical reactions of functional organic groups leading to the formation of chemical bonds [10]. POSS particles offer the possibility for the participation in curing by a reaction between POSS functional groups and the end or functional groups of polymer chains. The radicals generated during peroxide curing were used to initiate the grafting reactions between methacrylisobutyl-POSS and octavinyl-POSS and ethylene-propylene elastomer/hydrogenated acrylonitrile rubber EPM/HNBR blends [11]. The incorporation of octavinyl-POSS particles, which were able to form crosslinks between both rubbers, enhanced the compatibility of EPM/HNBR blend. Glycidyl polyhedral oligomeric silsesquioxane POSS was utilized as a crosslinking additive to prepare an organic-inorganic hybrid material based on the carboxyl-terminated poly(acrylonitrile-*co*-butadiene) [12]. In this work the trisilanolisobutyl-POSS and glycidyl-POSS were incorporated into the epoxidized natural rubber/poly(lactic acid) blend to enhance the mechanical, thermal, and oxidative properties. The influence of both POSS molecules on the thermo-oxidative degradation of polylactide is analyzed.

2. POSS structures as reinforcing additives to poly(lactic acid)

Thermoplastic material such as poly(lactic acid) usually is processed into fiber and films. Likewise many other aliphatic polyesters are an emerging polymer from renewable sources. In general, PLA is biodegradable and nontoxic for human body and thus is used for implantable composites, controlled drug release, food-packaging materials, and systems for sustained release of pesticides and fertilizers [13]. The high strength, modulus, and biodegradation make PLA a promising material for the production of packaging materials, although the brittleness restricts its large-scale application as an environmental friendly plastic product. Due to the chirality of lactic acid, various forms of polylactide exist as poly(L-lactide) PLLA or PLA, poly(D-lactide) PDLA, poly(D,L-lactide) PDLA, and poly(L-lactide-*co*-D,L-lactide) PLDLLA, which vary in properties [14–16]. PLLA is the product of L,L-lactide polymerization. It has a glass transition temperature T_g in a range of 50–65°C, a melting temperature of about 173–178°C, a crystallinity of around 37%, and a tensile modulus between 2.7 and 16 GPa [17, 18]. The blending of PLLA with PDLA allows the increase of the melting temperature and the temperature stability of the blend; additionally PDLA acts as a nucleating agent increasing the crystallization rate [14, 19, 20]. Biodegradation of the polylactide occurs due to a simple hydrolysis as the main degradation mechanism; thus it depends on the chirality of various PLA forms, and it is slower for PDLA because of the higher crystallinity [21].

Various methods were applied to obtain the POSS/poly(lactic acid) composites, among them are the solution casting method [22], the melt blending method [23–27], and injection molding [28].

These reports confirmed that the incorporation of various POSS particles had a reinforcing effect on the polylactide PLA properties. The crucial significance of the chemistry, reactivity, or non-reactivity of the functional POSS groups was

observed. These groups can control and enhance the compatibility between POSS and poly(lactic acid) leading to the better mechanical performance.

Octaisobutyl-POSS, aminopropylisobutyl-POSS, trisilanolisobutyl-POSS, and glycidylisobutyl-POSS/poly(ethylene-glycol) plasticized PLA composites, having various POSS content (1, 3, 7, and 10 wt%), were prepared [28]. The presence of different functional groups in POSS structure affected the dispersion and hence the mechanical properties of composites. Kodal et al. [28] reported the enhancement of the impact strength. Toughness of the plasticized poly(lactic acid) was significantly affected by the incorporation of POSS particles leading to the increase of the elongation at break. Moreover, it was revealed that regardless of POSS type, the melt viscosity of the composites decreased, in particular for the glycidylisobutyl-POSS. The presence of functional groups and its polarity was a crucial factor influencing the compatibility between POSS and polymer leading to the changes in mechanical performance. With the increasing POSS amount (from 1 to 10 wt%) incorporated into the polymer matrix, the tensile modulus of POSS/PEG/PLA composites decreased due to the worse dispersion of POSS particles at higher loading. Opposite the elongation at break, the energy at break and Izod impact strength meaningfully increased, indicating better toughness of the material after the incorporation of POSS particles.

A poly(ethylene glycol)-POSS containing long and flexible PEG segments attached to the inorganic core were prepared and applied to modify the brittleness of PLA [29, 30]. The toughening effect of PEG-POSS was observed [30]. The stress-strain curves of neat PLLA showed the typical brittle polymer tensile behavior, whereas for the PLLA containing 10 wt% of PEG-POSS, the shape of the curve was changed to atypical for ductile polymers. The tensile strength of the PEG-POSS/PLLA was reduced from 41.4 (neat PLLA) to 21.6 MPa; simultaneously the elongation of break increased from 8.7 (neat PLLA) to 21.6% [30]. The effect was attributed to the higher chain mobility of the PEG-POSS/PLLA composites as a PEG-POSS particles acted as an efficient plasticizing agent.

Zhang et al. [31] investigated the mechanical properties of octa(3-chloropropylsilsesquioxane)/PLLA hybrid films containing 3, 5, 10 and 15 wt% of incorporated POSS. The octa(3-chloropropylsilsesquioxane) was dispersed at molecular level at 3 wt%; higher loading led to aggregation and the crystallization of POSS particles. The tensile behavior of the PLLA material changed. More ductile behavior instead of the brittle behavior was observed. Elongation of break increased significantly from 13.5 (neat PLLA) to 91.0% (PLLA), containing 15 wt% of POSS confirming that the PLLA matrix was more plasticized [31]. Furthermore the incorporation of POSS caused the shifting of the glass transition temperature T_g and the melting temperatures of the PLLA matrix to lower values of temperature.

PLA composites having various octaisobutyl-POSS content (1, 3, 7, and 10 wt%) were obtained using a twin-screw micro-compounder [24]. It was showed that the isobutyl groups present in POSS increased compatibility with PLA backbone groups resulting in higher homogeneity and the miscibility between both components. Additionally, Yilmaz et al. [24] demonstrated that the incorporation of the octaisobutyl-POSS affected two components of total fracture work: essential work of fracture (the work spent in the inner fracture process zone) and nonessential work of fracture (the work spent in the plastic deformation zone). The unstable and rapid crack growth occurred suddenly after the maximum load in the neat PLA. The presence of octaisobutyl-POSS in PLA matrix raised the ductility of the composite, resulting in a stable crack growth for all POSS loadings. The greater energy absorption, the enhancement in toughness, and the increased extension to break without a significant loss of Young's modulus were attributed to the plasticization of PLA caused by the presence of octaisobutyl-POSS. The chain mobility of PLA was facilitated, as confirmed by the reduction in the glass transition temperature T_g of composites [24].

It was found also that the addition of octaisobutyl-POSS (5 wt%) led to the enhancement of the storage modulus (E′) below the glass transition temperature T_g; as compared with neat PLLA, the values of E′ increased from 1875 (neat PLLA) to 2485 MPa POSS/PLLA composite at 20°C [22]. The segmental motions of polymer chains in POSS/PLLA composite were not restricted, and no significant shift of the glass transition temperature T_g was observed [22].

Turan et al. [23] observed the plasticizing effect of POSS containing seven isobutyl groups and one functional aminopropyl group on PLA. Aminopropylisobutyl-POSS (1, 3, 10 wt%) reduced the melt viscosity of PLA composites. The power consumption during melt processing lowered as the processing was facilitated. This could be the additional advantage of POSS application. Tensile strength studies showed that the lower 1, 3 wt% content of aminopropylisobutyl-POSS enhanced Young's modulus. As the POSS content increased to 3 wt%, the modulus increased to 40% [23]. On the other hand, the incorporation of aminopropylisobutyl-POSS reduced the strain at break and yield point of PLA composites [23].

The formation of covalent bonds and physical interactions via hydrogen bonds between POSS and PLA chains usually lead to the enhancement of dynamic mechanical properties of POSS/PLA composites. This effect was observed for aminopropylisobutyl-POSS/PLA composites [23] up to 3 wt% of POSS content due to the physical (H-bonding) interactions of PLA chains with—NH_2 functional groups [23]. Higher content (10 wt%) of POSS particles caused the deterioration of dynamic mechanical properties resulting from the agglomeration of the filler.

In order to improve the compatibility and lead to better mechanical properties, the hybrid POSS-PLLA nanoparticles with different tail lengths were incorporated to neat PLLA. PLLA/POSS nanocomposites, in which the PLLA chains were grafted onto the POSS molecules, were prepared via microwave-assisted ring-opening polymerization [32]. The interfacial compatibility was strongly affected by the length of grafted PLLA chain and the amount of PLLA-POSS added. The addition of 6 wt% of PLLA-POSS with the longest grafted PLLA tail leading to effective nucleation activity and the improvement of Young's modulus by 57% and the tensile strength by 26.5%. Other authors [33] observed simultaneous enhancement in toughness and strength for polylactide containing octa-armed polyhedral oligomeric silsesquioxanes POSS-$(PLLA)_8$ star hybrid particles.

The ability to increase the compatibility between components of blends is another important factor that the application of POSS offers.

Blends of poly(lactic acid) PLA, triallyl isocyanurate, and octavinyl-POSS were prepared and cured by γ-irradiation [27]. The presence of the unsaturated functional groups in POSS structure provided the possibility of the grafting of POSS moieties to the PLA chains. The crosslinking occurred together with the degradation processes. The chemical bonds were formed between the double bonds of POSS particles and the polymer radical generated during γ-irradiation exposure. Due to the higher crosslink density of octavinyl-POSS/PLA composites the tensile strength, E-modulus, and the heat deflection temperature increased. The glass transition temperatures of POSS/PLA composites were shifted to higher temperature confirming the formation of more cross-linked network in the presence of octavinyl-POSS.

Other authors [25] incorporated 2 and 5 wt% of octavinyl-POSS and epoxycyclohexyl-POSS to blend prepared by mixing of poly(lactic acid) and poly(butylene succinate-co-adipate). PLA/PBSA blend was prepared using a fixed weight ratio of 70:30 of both components [25]. The opposite effects of both POSS on the viscoelastic properties, the storage modulus and complex viscosity, were observed. Octavinyl-POSS acted as a plasticizing additive, reducing the melt elasticity and decreasing the values of the storage modulus and complex viscosity. The epoxycyclohexyl group of POSS reacted with the functional groups present at the end of

PLA/PBSA chains leading to the enhancement of the storage modulus and higher compatibility of the blend.

Octaisobutyl-POSS and trans-cyclohexanediolisobutyl POSS containing functional hydroxyl groups potentially that are able to interact with both polymer matrices were added at 2 wt% loading to poly(lactide) and poly(ε-caprolactone) blend by melt blending method [34]. Moreover, to enhance the POSS adhesion to the components of the blends, authors [34] grafted the PCL-*b*-PLLA block copolymer onto the aminopropyl heptaisobutyl-POSS molecules via ring-opening polymerization of ε-caprolactone and $_{L}$-lactide. The functionalized POSS molecules were found to be compatibilizing agent able to stabilize the morphology of PLA/PCL blends [34].

The compatibilizing and stabilizing effect of various particles reported in literature can be attributed to the decrease of the interfacial energy; the localization of the solid particles at the interphase between two polymers, acting as a solid barrier preventing the coalescence; the strong interactions with polymeric chains bringing about the steric hindrance; and the change in the viscosity ratio resulting from the uneven distribution of filler particles in both phases. Monticelli et al. [34] reported that the octaisobutyl-POSS was preferentially located in PCL phase resulting in the increase of polymer viscosity. Higher viscosity reduced the coalescence leading to the reduction of the PCL droplets size. Trans-cyclohexanediolisobutyl POSS because of its higher functionality and affinity to both phases was able to locate at the interphase leading to stronger interfacial adhesion of both components in PLA/PCL composite.

Han et al. [35] reported the compatibilizing effect of Janus POSS star hybrid, which contained an inorganic POSS core and three poly(ε-caprolactone) arms and five poly($_{L}$-lactide) arms, on the PLLA/PCL (w/w = 70/30) blends. Due to the reduction in interfacial tension, the dispersed PCL domain size decreased from 1 to 0.5 μm. Better compatibility caused by POSS star particles led to the increase of the Izod impact strength and tensile mechanical properties.

The reduced interfacial tension in poly(lactic acid)/starch/poly(ε-caprolactone) blends after the incorporation of the trifluoropropyl-POSS particles (1, 3, 5 wt%) was also the main factor leading to the enhanced compatibility of the system [26].

Summarizing the application of various POSS molecules, it is worth to underline that the reinforcing effect of POSS molecules is strongly dependent on the chemistry of the organic groups present in the filler structure. The compatibility between the POSS and PLA can be enhanced by the presence in POSS backbone aliphatic groups with higher affinity to polymer chains. These groups can facilitate mixing between polymer and filler during processing reducing, uneven dispersion of filler in matrix and leading to higher homogeneity. Thus the better dispersion improves mechanical properties. On the other hand, more polar groups, in particular glycidyl, epoxy, or hydroxyl groups, can form physical interactions or even covalent bonds with the end groups of PLA, causing the improvement of dynamic mechanical properties.

Herein we decided to apply POSS molecules containing isooctyl, hydroxyl, and glycidyl functionalities as an additive to epoxidized natural rubber PLA blends.

3. Influence of POSS on crystallinity, thermal stability, and degradation of poly(lactic acid)

PLLA is a semicrystalline polymer; thus its crystallization behavior and degree of crystallinity are important factors playing a vital role in various properties, e.g., mechanical, thermal, and degradation properties. A large number of studies are reported in the literature related to the crystallization of poly(lactic acid) [36–39]. The crystallization kinetics [40], the influence of the molecular weight and undercooling on morphology and crystal grow [41], and the isothermal

melting mechanism [42] were investigated. PLA crystallization, even at high L-LA content, is typically too slow; thus, to increase the crystallinity, three main strategies can be considered: the incorporation of a nucleating agent, the addition of a plasticizer, and the adjustment of the molding conditions, in particular molding temperature and cooling time. Talc is usually used as a nucleating agent that lowers the surface-free energy barrier toward nucleation, increasing the crystallization rate [39].

Some authors reported a nucleating influence of aminopropylisobutyl-POSS particles on the crystallization [23]. The effect was confirmed by the enhanced degree of crystallinity and lower cold crystallization temperatures for PLA composites containing 3 and 10 wt% of POSS [23].

Wang et al. [25] showed that octavinyl-POSS, and epoxycyclohexyl-POSS can act as nucleating agents, enhancing the crystallization ability of poly(lactic acid) in PLA/PBSA blends. Additionally both incorporated POSS increased the decomposition temperature retarding the thermal degradation of PLA/PBSA blends.

Qiu et al. [22] investigated poly(L-lactide)/octaisobutyl-POSS nanocomposites prepared via solution casting method. The crystallization studies revealed that 5 wt% of octaisobutyl-POSS increased the degree of crystallinity from around 14.8% for neat PLLA to around 43.2% for the PLLA/octaisobutyl-POSS composites. Octaisobutyl-POSS reduced the half time of crystallization $t_{0.5}$ defined as the time required to achieve 50% of the final crystallinity for the sample. The nucleation density was enhanced in the PLLA/octaisobutyl-POSS composites compared with that of neat PLLA. Octaisobutyl-POSS increased the values of weight loss with prolonged exposure time, indicating the accelerating effect of the POSS particles on the hydrolytic degradation of PLLA in composite.

Other authors [28] also reported the influence of POSS with octaisobutyl, amine, hydroxyl, and epoxide groups on the crystallization behavior of PEG-plasticized PLA. All POSS types reduced the cold crystallization temperature T_{cc}, leading to much faster nucleation rate of POSS-filled PLA and PEG-plasticized PLA. Furthermore the POSS addition shifted the glass transition temperature of PLA phase to lower value of temperature due to the plasticization of PLA matrix. The strongest plasticizing effect was observed for octaisobutyl-POSS. All utilized POSS particles enhanced the thermal stability acting as a physical barrier which reduced the heat flow to the matrix and increased the decomposition temperatures at 5%, 10%, and maximum weight loss.

Yu and Qiu [43] studied the crystallization behavior, spherulitic morphology, and crystal structure of poly($_L$-lactide) mixed via solution casting method with two different weight ratios (0.5, 1 wt%) of octavinyl-POSS. Both the nonisothermal melt and cold crystallization of PLLA were enhanced by the presence of octavinyl-POSS presence, to the higher degree of crystallinity χ_C = 44.4% for 1 wt% of octavinyl-POSS compared to χ_C = 8.0% for neat PLLA. The overall crystallization rates during isothermal crystallization were faster and improved with increasing octavinyl-POSS content. The time to achieve the 50% progress of crystallization shortened, and the calculated values of $t_{0.5}$ were lower for octavinyl-POSS/PLLA composites confirming that the crystallization of PLLA was accelerated in the presence of POSS particles. No significant changes in the crystallization mechanism were found, although the number and the size of developed spherulites changed indicating the nucleating effect caused by the POSS particles. The nucleation density of PLLA spherulites increased significantly in the octavinyl-POSS/PLLA in respect to the neat PLLA. The neat PLLA and octavinyl-POSS/PLLA composites showed a similar degradation profile. The degradation temperatures at 5% of weight loss and the decomposition temperatures were reduced slightly after the incorporation of octavinyl-POSS particles [43].

Similar effect on crystallinity was reported for the PLLA composites containing various octa(3-chloropropylsilsesquioxane) content [31]. Studies indicated that octa(3-chloropropyl)-POSS can be an effective heterogeneous nucleating agent promoting the crystallization of PLLA and increasing the degree of crystallinity.

The low concentration of fluorinated POSS particles (0.5 wt%) was found to be a suitable nucleating agent, increasing the crystallinity of PLA in PLA/starch/PCL blend [26]. At a low concentration POSS acted as a lubricating agent that lowered the viscosity of polymer melt which had the positive effect on the nucleation and growth stages. At higher POSS concentration the increased viscosity of the system had an adverse influence on the growth of spherulites [26].

As we previously described, silsesquioxanes with reactive functionalities are suitable for polymerization, surface bonding, or grafting. The POSS molecules containing hydroxyl groups could be adopted as initiators of the ring-opening polymerization ROP during the synthesis of PLA from lactide. Organic-inorganic hybrids with various arms' length of poly(lactic acid) tethered with POSS synthetized via ring-opening polymerization of L-lactide were found to be nucleating additives increasing the degree of crystallinity of PLA [32, 33].

Similar to other aliphatic polyesters, PLA is able to degrade during processing because of the action of the external factors. Polymer degradation can occur due to the influence of the temperature (thermal degradation), the effect of the presence of oxygen, and the elevated temperature (thermo-oxidative degradation), as a result of the mechanical stress (thermomechanical degradation). During the processing at the elevated temperature (usually in temperature range of 180–200°C), the thermo-oxidative degradation can lead to the random chain scission and the formation of degradation products [44].

POSS molecules were found to be the additives which according to the chemical structure can both accelerate or postpone the thermal degradation of PLA composites. The influence of the octaisobutyl-POSS and the accelerating effect of POSS incorporation on the hydrolytic degradation of POSS/PLLA nanocomposite with respect to neat PLLA were reported [22]. Octavinyl-POSS caused the opposite effect leading to the higher thermal stability and the delay in oxidation of PLA [45].

4. Materials and characterization

L-polylactide PLA, CAS number 331335-50-1 product of Simagchem Corporation (China) was applied as a dominant component of the poly(lactic acid)/epoxidized natural rubber blends, the formulations of the blends were as follows:

100 g PLA—ENR 75 g, further denoted as 75 ENR/PLA blend
100 g PLA—ENR 50 g, further denoted as 50 ENR/PLA blend
100 g PLA—ENR 25 g, further denoted as 25 ENR/PLA blend

In this study the epoxidized natural rubber ENR50 (Epoxyprene 50, Muang Mai Guthrie Company) was used.

A liquid glycidyl-POSS cage mixture EP0409 (Hybrid, USA), further denoted as Gly-POSS, with an inorganic silsesquioxane core and eight glycidyl groups attached to the corners of the cage; characterized by the properties (e.g., epoxy equivalent weight 167; thermal stability (5 wt% loss) 365°C; and a liquid trisilanolisooctyl-POSS SO1455 (Hybrid, USA)); further marked as HO-POSS, an open cage POSS with seven isooctyl groups attached at the corners of the cage and three active silanol (hydroxyl groups) functionalities; and characterized by thermal stability (5 wt% loss) 363°C was applied as an additive at 3 wt% to the 50 ENR/PLA blend.

Additionally, the PLA formulations containing 3 wt% of Gly-POSS and HO-POSS, with properties described above were prepared.

Before the preparation of the PLA blends, the oven drying at 80°C during 24 h for polymer pellets was done. ENR/PLA blends were prepared by melt mixing in Brabender Lab Station Plasti-Corder, a small laboratory mixer with counter-rotating rotors. First the PLA pellets were placed in a mixing chamber and melted at 180°C. After 5 min the appropriate amount of epoxidized rubber was added. In the case of ENR/PLA/POSS blends, the appropriate amount (3 wt%) of Gly-POSS or HO-POSS, respectively, was added to PLA before the epoxidized rubber. The composition was mixed during 5 min at 150 rpm of rotor speed and then removed from mixer. After the mixing blends were again preheated at 180°C for 2 min and transferred to a mold, they are pressed at 200 bar during 10 min to form films. Similar procedure was applied to prepare the samples of PLA containing 3 wt% of various POSS molecules.

The tensile strength TS and the elongation at break of samples were measured according to ISO 37:2005 standard using universal testing machine Zwick Roell 1435 at room temperatures. The films were shaped into specimens by dumbbell-shaped cutter. The width and the length of the gauge region of the specimens were 4 mm and 25 mm, respectively. The speed of crosshead was 100 mm min^{-1}. The average values of six measurements were taken for each sample. The changes in mechanical properties after the degradation in soil during 1 month under controlled aging conditions (temperature 50°C, humidity 90%, pH = 5.5) were determined.

The dynamic viscoelastic properties of PLA/ENR blends at ambient temperatures were investigated using oscillation rheometer Ares G2 (TA Instruments) equipped with parallel-plate geometry (diameter of 25 mm). The oscillation amplitude sweep tests at temperature 25°C and constant angular frequency of 10 rad s^{-1} were conducted in oscillation strain range from 0.001 to 50%. Storage shear modulus G′, loss shear modulus G″, and loss tan δ were analyzed. Studies of thermo-oxidative degradation were done using Ares G2 equipment, the samples were degraded at 180°C during 0, 30, 60, and 120 min under air atmosphere (flow rate 1 L min^{-1}), and then a frequency sweep tests at low oscillation strain (linear viscoelastic region) from 1 rad s^{-1} to 628 rad s^{-1} were performed.

The fitting of the storage shear modulus G′ and the loss shear modulus G″ values to Maxwell's equations (4) and (5) and the calculation of the discrete relaxation spectrum were done by the TRIOS® Software provided by TA Instruments.

DSC analysis was performed using DSC1 apparatus (Mettler Toledo). All tests were performed under nitrogen atmosphere. The samples were subjected to two heating steps from 20 to 210°C, with a heating rate of 10°C/min. The objective of the first heating step was to eliminate the heat history of the sample.

The analysis of blend morphology was done using SEM microscope (JEOL Sendai Japan) for the fracture surface covered by gold. The ENR phase in 50 ENR/PLA samples was removed before the test by dissolving in toluene during 72 h.

5. Influence of Gly-POSS and HO-POSS on mechanical properties and crystallization of PLA/ENR blends: changes in mechanical performance of the blends after degradation in soil

The brittleness of PLA can be improved by elastomeric toughening additives. The polyisoprene rubber (IR), silicone rubber (SI), and acrylic rubber (AR) were used as a second component of the PLA blend to improve the mechanical performance of poly(lactic acid) [46]. Among all these blends, PLA/polyisoprene possessed high-tensile toughness due to its rubbery characteristic but low degree of crystallinity. Opposite the incorporation of acrylic rubber led to higher degree of crystallinity but quite low

toughness. The toughness of PLA has been improved by the incorporating core-shell rubber particles [47]. It was found that the impact strength and the elongation at break increased without deterioration of thermal properties of final material. A matrix/dispersed morphology of various acrylonitrile content acrylonitrile-butadiene rubber/PLA blends was reported [48]. It was concluded that the incorporation of 10 wt% of rubber resulted in the enhancement of toughness and impact strength of neat PLA without any reduction in crystallinity. Desa et al. [49] investigated properties of PLA toughened by the addition of natural rubber (NR) and epoxidized natural rubber (ENR), after the addition of 5 wt% of rubber the impact strength of PLA increased from 3.35 kJ m^{-2} to 4.52 kJ m^{-2} (NR) and 4.14 kJ m^{-2} (ENR). The decrease of PLA crystallinity after incorporation of both rubbers was observed.

Since mechanical properties of immiscible polymer blends depend strongly on the formed morphology the analysis of SEM images was applied to observe the microstructure of the ENR/PLA. **Figures 1–4** display the changes in the microstructure of the blends. The EPM phase was dissolved and removed. The voids indicate the areas where the ENR phase was previously present. All blends showed phase separation confirming immiscibility of both phases. The droplets of ENR were dispersed throughout the PLA matrix. The PLA blend with 25 wt% of rubber characterized the smaller size of the elastomer domains. The increase of rubber loading up to 50 wt% resulted in higher melt strength during blend preparation at 180°C, retarding the rubber particle rupture during mixing consequently increasing the size of the rubber droplets in ENR/PLA blend. The elongated shape of rubber phase droplets was observed for the PLA blend containing 75 wt% of ENR. The addition of HO-POSS with isooctyl groups decreased the interfacial tension between the components of 50 ENR/PLA blend; as a consequence, the melt blending process was facilitated. The breakdown of rubber droplets was favorable leading to the better dispersion of rubber particles in PLA.

Dynamic mechanical characterization of obtained polymer blends at ambient temperature is able to give an additional insight onto the changes in mechanical performance after the incorporation of both POSS. Firstly, the attention of studies was focused on the effect of the various formulation of the ENR/PLA blend on the viscoelastic behavior; the changes of the storage shear modulus G′ as a function of oscillation strain at angular frequency of 10 rad s^{-1} were estimated (**Figure 5**). For the ENR/PLA composites, the storage shear modulus was found to be independent of strain up to low strain levels comparing to the neat uncured ENR rubber.

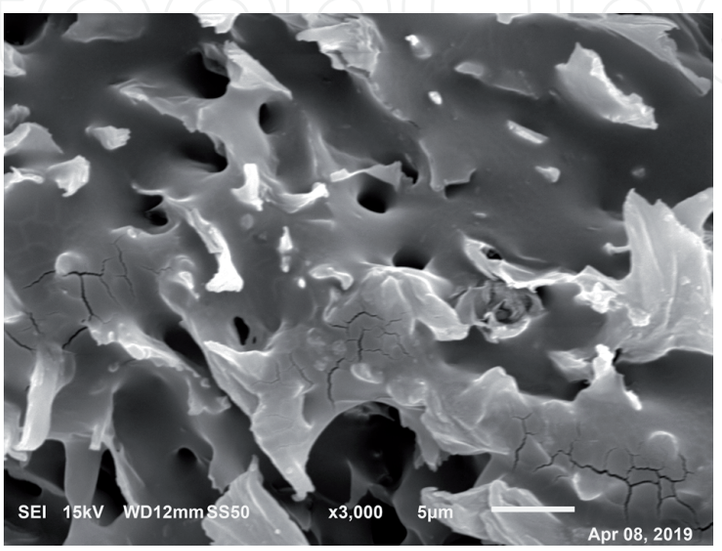


Figure 1.
SEM image of 25 ENR/PLA blend.

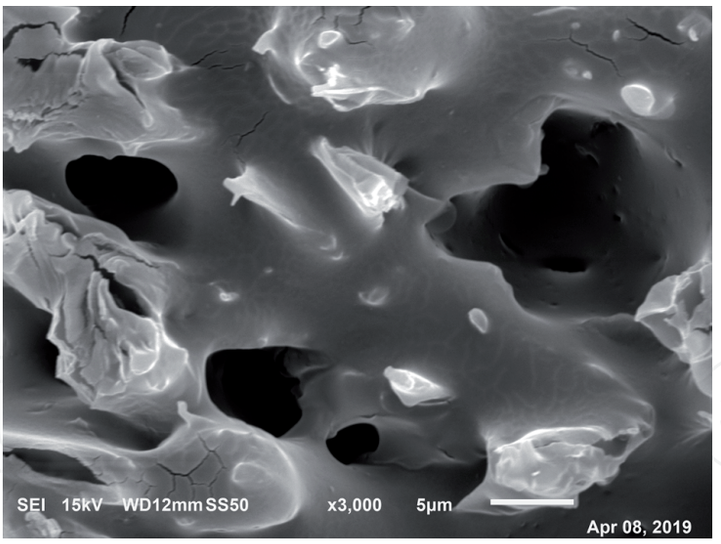


Figure 2.
SEM image of 50 ENR/PLA blend.

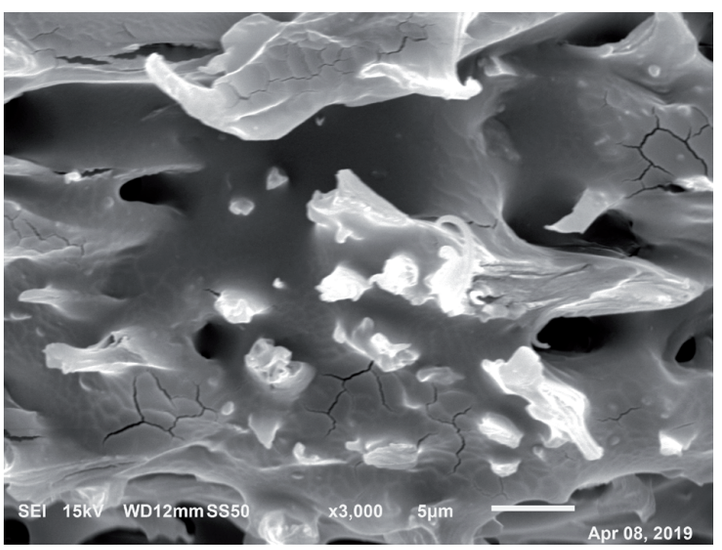


Figure 3.
SEM image of 50 ENR/PLA blend modified by HO-POSS.

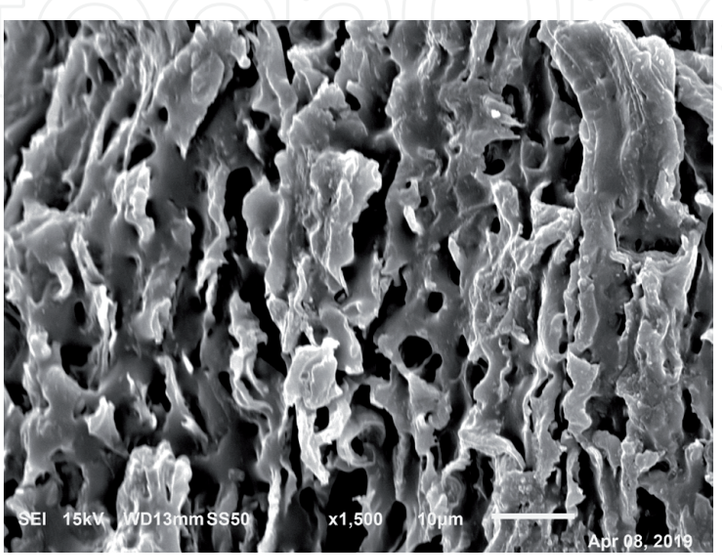


Figure 4.
SEM image of 75 ENR/PLA blend.

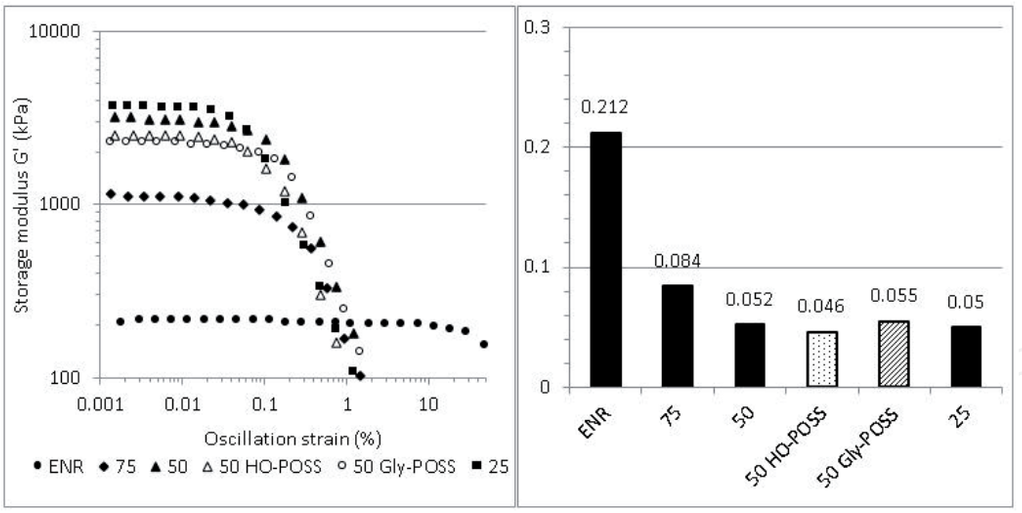


Figure 5.
Storage shear modulus G' as a function of oscillation strain (%) at 25°C for ENR/PLA blends with various ENR/PLA ratio (left). Damping properties and loss tan δ measured at linear viscoelastic region (oscillation strain of 0.01%, angular frequency of 10 rad s^{-1}, and temperature of 25°C) (right).

An increase of the oscillation strain above 0.2% caused strong decrease of storage shear modulus G′ for all formulations. As it was expected, the higher ratio of ENR in 75 ENR/PLA blend reduced significantly the values of storage shear modulus G′; at the same time, the loss tan δ increased, indicating stronger energy dissipation and better damping properties. It should be noted that both POSS molecules decreased the storage modulus G′ in comparison with neat 50 ENR/PLA blend. This effect can be attributed to a plasticization effect caused by the liquid Gly-POSS and HO-POSS, on the 50 ENR/PLA blend.

The more significant increase of the values of loss shear modulus as a function of oscillation strain was observed for 25 and 50 ENR/PLA blends (**Figure 6**). The higher applied force caused first the increase of the loss modulus G′ attributed to the higher dissipation of the energy, which resulted from the presence of the rubber phase in the blend, and then the microstructure of the blend collapsed leading to the decrease of both G′ and G″ moduli. Increasing the content of ENR in the blend caused the shift of the obtained maximum value of loss modulus G′ to a higher value of oscillation strain indicating that the formed microstructure was able to

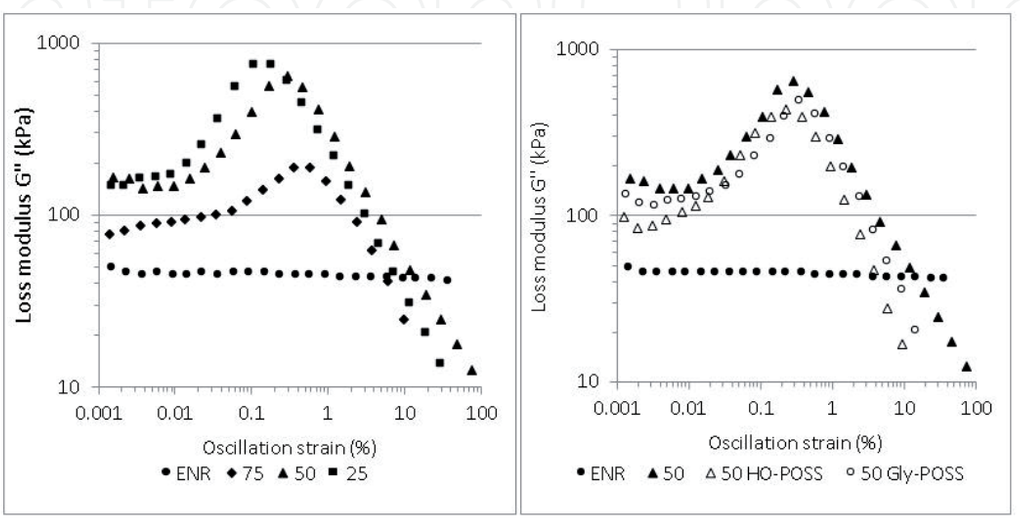


Figure 6.
Loss shear modulus G" as a function of oscillation strain (%) at angular frequency of 10 rad s^{-1} and temperature of 25°C for ENR/PLA blends with various ENR/PLA ratio.

dissipate the energy up to higher level of deformation. For the composition containing POSS molecules, the lower values of loss shear modulus G′ were observed.

The mechanical properties of PLA blended with various content of ENR rubber are shown in **Table 1**. As it can be seen, the increasing ENR content led to the decrease of tensile strength, simultaneously increasing the elongation of break. Comparing all blends containing 50 wt% of ENR rubber, the tensile properties enhanced after the incorporation of both POSS additives. As the tensile properties of a polymer blends are correlated with the micromorphology, the better dispersion of rubber droplets in PLA matrix and the extent of the interfacial adhesion caused by the presence of functional groups in POSS molecules are responsible for the tensile strength increase observed for 50 ENR/PLA blend after the incorporation of both POSS.

In order to be assimilated by the microorganism present in soil, degradable polymer material needs to be fragmented. Even for the biodegradable materials such as poly(lactic acid), the unintentionally disposal of polymeric material could generate problems. It should be taken under consideration that soils can vary from place to place. The soil characteristic (temperature, water content, chemical composition, and pH) strongly influences on the degradation [50]. Degradation of polymer occurs due to the presence of oxygen, water, atmospheric pollutants, and agrochemicals. Activity of water, pH, temperature, and time must be controlled because they are factors promoting the hydrolytic degradation of polymers containing hydrolysable covalent bonds such as ester bonds. Moreover, the ratio of crystallinity affects the oxidative and hydrolytic degradation. The crystalline domains can restrict the diffusion of oxygen and water, limiting the chemical degradation [51]. The presence of rubber particles can be another factor strongly influencing on the degradation of the ENR/PLA blend. It was reported in literature that the degradation of polymers containing unsaturated bonds or backbone groups can occur via processes leading to crosslinking reactions or chain scission [52].

The changes in mechanical properties of the ENR/PLA blends were determined after the degradation of the material in soil during 1 month (**Table 1**). Additionally to estimate the effect of rubber on the degradation of the ENR/PLA blend, the aging coefficient K_C was calculated according to Eq. (1):

$$K_C = \frac{(TS * E_b)_{aged}}{(TS * E_b)_{befor\ ageing}}, \quad (1)$$

where TS is tensile strength and E_b is the elongation at break. The observed for the neat ENR value of the K_c coefficient (higher than one) and the increase of the tensile strength after aging confirmed that during composting, because of the

Composition of PLA/ENR	TS (MPa)	E_b (%)	TS^* (MPa)	E_b^* (%)	K_C
Neat ENR	0.50 ± 0.04	399 ± 31	0.68 ± 0.05	369 ± 73	1.26 ± 0.05
Neat PLA	24.7 ± 0.9	2.1 ± 0.5	3.43 ± 1.10	0.4 ± 0.4	0.03 ± 0.01
25 ENR/PLA	20.7 ± 3.6	3.8 ± 0.9	9.21 ± 1.2	2.7 ± 0.6	0.32 ± 0.05
50 ENR/PLA	10.4 ± 0.9	4.4 ± 1.4	6.99 ± 0.82	2.7 ± 0.7	0.41 ± 0.04
50 Gly-POSS	**12.0 ± 0.6**	**4.7 ± 1.6**	**3.88 ± 0.53**	**1.8 ± 0.9**	**0.12 ± 0.03**
50 HO-POSS	**11.0 ± 0.9**	**4.7 ± 1.4**	**3.60 ± 0.83**	**3.5 ± 0.7**	**0.24 ± 0.03**
75 ENR/PLA	6.9 ± 0.9	7.1 ± 2.4	5.68 ± 0.91	4.3 ± 1.1	0.50 ± 0.04

Bolded values are for the samples of blend containing POSS

Table 1.
Mechanical properties, tensile strength TS (MPa), and elongation at break E_b (%) of PLA/ENR blends with various PLA/ENR ratio. Tensile strength TS^* and elongation at break E_b^* after composting. Calculated values of compositing coefficient K_C.

Composition of blend	T_g °C	T_{cc} °C	T_m °C	χ_c
Neat PLA	55.4	106.1	156.8	2.7
25 ENR/PLA	55.3	124.9	148.5	1.9
50 ENR/PLA	55.3	128.3	147.3	0.8
50 Gly-POSS	49.4	—	—	—
50 HO-POSS	54.5	125.6	147.1	1.5
75 ENR/PLA	55.9	105.7	146.8	0.1

Table 2.
DSC analysis of ENR/PLA composites.

presence of unsaturated >C═C < bonds, the crosslinking occurred. In comparison with the neat PLA, the incorporation of rubber increased the values of K_C parameters, although lower than one values of the K_c parameter indicated that the partial degradation occurred. The changes in the microstructure of the blend caused by the degradation of PLA phase resulted in the deterioration of mechanical properties and in the decrease of the tensile strength TS and the elongation of break E_b of blend. The incorporation of Gly-POSS accelerated significantly the aging process, and lower value of K_c parameter was observed compared with 50 ENR/PLA blend. The decrease of K_c parameter resulted from the plasticizing influence of the liquid-like POSS on the PLA phase and the lower amount of crystalline phase. Both factors improved the diffusion of water and oxygen throughout the material, accelerating the degradation. Observations were confirmed by the degree of crystallinity calculated according to Eq. (2) [48]:

$$\chi_C = \frac{\Delta H_m - \Delta H_c}{w_{PLA}\,\Delta H_m^{\circ}}, \tag{2}$$

where ΔH_m and ΔH_C are the enthalpies of melting and cold crystallization during the second heating cycle, respectively; ΔH°_m is the enthalpy of 100% crystalline PLA homopolymer (93.7 J g^{-1}) [53]; and w_{PLA} is the weight fraction of PLA component in the blend (**Table 2**). The degree of crystallinity was calculated for the second cycle of heating, after erasing the thermal history of samples. During cooling no crystallization was observed. The crucial factor influencing the ratio of degradation in soil for 50 ENR/PLA blend modified by Gly-POSS in comparison with not modified 50 ENR/PLA blend and modified by HO-POSS was the amorphous structure and absence of crystalline phase. It should be also underlined that significant decrease in degree of crystallinity is observed for each ENR/PLA blend. The higher the amount of rubber, the lower the percentage of crystallization. Similar influence of epoxidized rubber on PLA was reported by Desa et al. [49].

6. Influence of POSS on the thermo-oxidative degradation of neat PLA and ENR/PLA blends

It is well known that the dynamic oscillatory measurements are very sensitive and allowed to characterize the changes occurred in the structure of melted polymers.

Different POSS were reported to be able to retard the changes of material properties occurring during processing; for this reason, the viscoelastic rheological characterization at 180°C was investigated to estimate the influence of POSS molecules on melt properties.

Figure 7 displays the evolution of complex viscosity as a function of angular frequency. It can be seen that η^* of the ENR/PLA blends containing higher rubber loading increased. Further, analyzing the influence of POSS incorporation the powerful influence of HO-POSS on η^* is observed for the whole frequency range in comparison with neat 50 ENR/PLA blend. The viscosity of POSS-polymer composite depends on the level of interactions. HO-POSS because of the presence of hydroxyl groups as well as isooctyl groups has higher affinity to both phases of the blend. Higher level of physical interactions between the polymer chains and HO-POSS resulted in increased viscosity of the melt in comparison with neat 50 ENR/PLA. This effect was not observed in case of Gly-POSS. As shown in **Figure 7** the thermo-oxidative degradation during 30 min led to the continuous increase of the complex viscosity of blends containing higher content of ENR rubber. The temperature probably caused the partial curing of the ENR phase. Additionally the formation of covalent bonds between hydroxyl groups present at the end of PLA chains and the epoxy groups of ENR was possible under these conditions of aging. Therefore all these reactions led to the changes in the polymer structure resulting in the formation of more branched structures and in the increase of the molecular weight. Taking into account that all degraded at 180°C samples showed during 30 min the increase of the complex viscosity η^* to quantify the effect of POSS for various degradation times, a relative degradation index RDI (3) was calculated according to the equation:

$$R.D.I = \frac{\eta_{time=0}}{\eta_{time}}, \tag{3}$$

where $\eta_{time = 0}$ is the complex viscosity value at 1 rad s^{-1} for a sample not degraded and η_{time} is a the complex viscosity at 1 rad s^{-1} after 30, 60, and 120 min of thermo-oxidative degradation at 180°C. Hence, the parameter allows to quantify the increase in the melt viscosity due the crosslinking reactions or the formation of more branched structures with higher molecular weight (values lower than 1) or the drop of melt viscosity resulting from the chain scission (values higher than 1). The calculated values of RDI indexes for ENR/PLA POSS composites are compiled in **Figure 8**. The significantly lower values of RDI indexes observed for neat 50 ENR/PLA and Gly-POSS 50 ENR/PLA indicate that an increase of the melt viscosity occurred in higher extent than the HO-POSS 50 ENR/PLA blend. The increase in η^* at intermediate

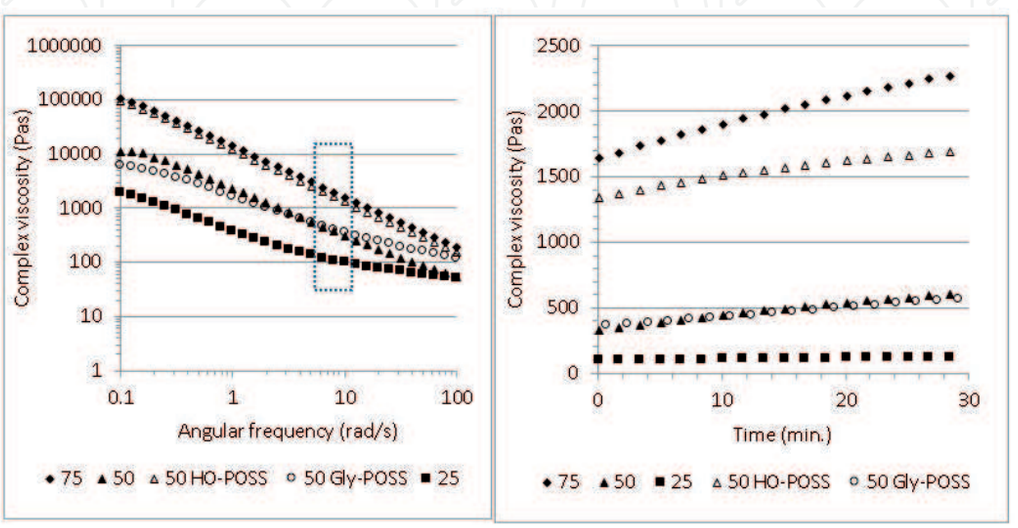


Figure 7.
Complex viscosity η as a function of angular frequency ω at 180°C (left). Complex viscosity as a function of time during 30 min of thermo-oxidative aging at 180°C (right).*

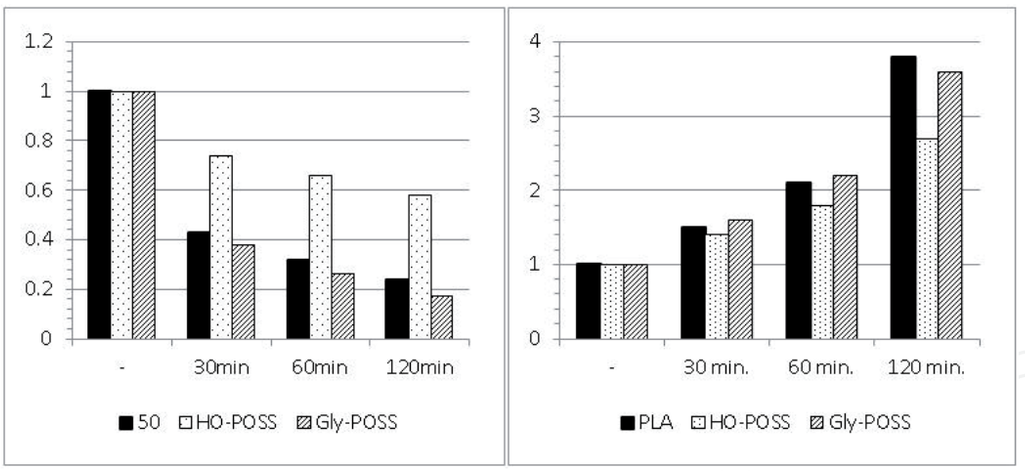


Figure 8.
Values of RDI indexes for the ENR/PLA blend (left) and PLA (right) modified by HO-POSS and Gly-POSS.

frequencies can relate to a restriction in chain mobility caused by chain branching or curing of ENR phase. During thermo-oxidative degradation of the melt blend, the total amount of the hydroxyl groups present at the end of the PLA chains increased, causing higher possibility to react with epoxy groups present in ENR. Comparing both POSS molecules, the weaker influence of HO-POSS on the increase of melt viscosity during thermo-oxidative degradation is observed. HO-POSS contains three silanol groups potentially able to react with epoxy functionalities of ENR, but these groups are covered by the isooctyl groups linked to the same silicon atom reducing the probability of the covalent bond formation with polymeric chains due to the steric hindrance. Moreover the higher melt viscosity of HO-POSS 50ENR/PLA blend (**Figure 7**) in comparison with neat 50 ENR/PLA formulation reduced the diffusion of oxygen preventing the degradation of both phases during processing.

Additionally **Figure 8** displays the evolution of RDI indexes for the neat PLA and PLA modified by 3 wt% of HO-POSS and Gly-POSS. All degraded samples presented similar behavior, which is typical for the thermo-oxidative degradation of PLA. The longer degradation time caused a decrease in melt viscosity, indicating the chain scission that was confirmed by the continuous increase of the RDI indexes after longer period of time. However, as for HO-POSS PLA, it can be indicated from **Figure 8** that the longer time of degradation favored the chain scission and decrease of melt viscosity, but the obtained viscosity reduction was restricted in comparison with neat PLA. Similarly, a reduction in values of RDI index after 120 min of thermo-oxidative degradation after incorporation of Gly-POSS is observed compared with neat PLA. Both POSS molecules enhanced the thermo-oxidative stability of neat PLA, although more significant stabilizing effect occurred for the HO-POSS. To analyze more deeply the influence of POSS molecules on the rheological behavior, the changes of storage modulus G′ and loss modulus G″ after thermo-oxidative aging during various times were determined. As an illustrative example, the evolution of both viscoelastic moduli as a function of frequency for 50 ENR/PLA blend is showed in **Figure 9**. As can be observed, all degraded samples of 50 ENR/PLA blend during various times of 30, 60, and 120 min showed predominant elastic behavior with storage modulus values G″ higher than loss modulus values G″ in whole studied frequency range. The thermo-oxidative degradation led to the increase of both moduli G′ and G″, and the increment of both moduli was dependent on the time of degradation. This fact pointed out that a degradation under this condition showed similar qualitative response, but the quantitative effect varied according to the time of degradation and was more accelerated during the first 30 min of degradation.

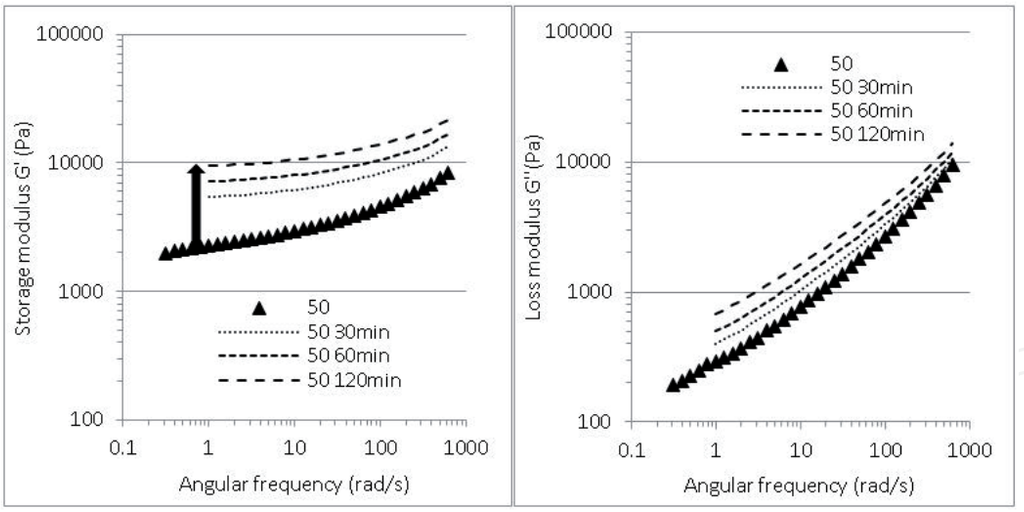


Figure 9.
Influence of the thermo-oxidative aging (30, 60, 120 min) on the viscoelastic properties (storage modulus G', loss modulus G") as a function of angular frequency at 180°C for 50 ENR/PLA blend.

For HO-POSS 50 ENR/PLA blend, when increasing degradation time, both moduli increased (**Figure 10**); regarding the increment of the G′ and G″ moduli, the presence of POSS molecules slowed the degradation of the blend. Interestingly, the opposite effect was observed for Gly-POSS 50 ENR/PLA; the degradation led to remarkable increase of the G′ modulus and decrease of the G″ modulus, indicating that the curing reactions occurred in higher extent. These results confirmed the observation from the analysis of melt viscosity and RMI indexes.

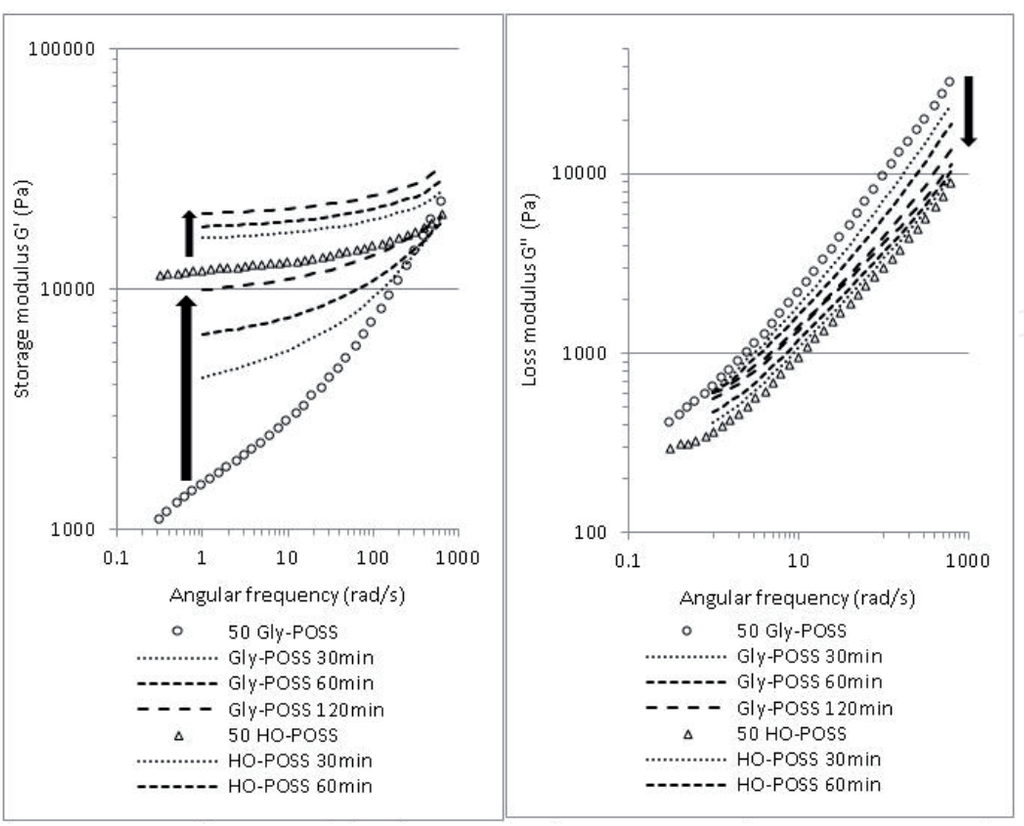


Figure 10.
Influence of the thermo-oxidative aging (30, 60, 120 min) on the viscoelastic properties (storage modulus G', loss modulus G") as a function of angular frequency ω for the POSS-modified PLA/ENR blends at 180°C.

The plasticizing effect of Gly-POSS on PLA was confirmed, and the addition of 3 wt% of Gly-POSS caused the decrease of the melt viscosity (not showed here); additionally lower values of storage modulus G′ were observed, indicating the decrease in chain entanglement and more free volume in the melt (**Figure 11**). For the PLA composites containing POSS molecules when increasing the degradation time, both moduli underwent a drop, and the effect was less predominant in the case of HO-POSS; thus, these investigations confirmed better thermal stability of HO-POSS formulation comparing with neat PLA.

The linear viscoelasticity data were used to obtain the discrete relaxation spectrum, which provides additional information about possible changes in PLA structure occurring during thermo-oxidative degradation. A discrete relaxation spectra is described by the generalized Maxwell model by the following relationships (4, 5) [54]:

$$G'(\omega) = \sum_{i=1}^{N} G_i \frac{(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2} \tag{4}$$

$$G''(\omega) = \sum_{i=1}^{N} G_i \frac{(\omega\lambda_i)}{1 + (\omega\lambda_i)^2} \tag{5}$$

where G_i and λ_i are the relaxation strength and relaxation time, respectively. It was found that for the experimental frequency range used in studies, the six Maxwell elements are sufficient for recalculation of the values of storage G′ and loss G″ moduli with high level of correlation (R^2 = 0.999). **Figure 12** presents the discrete relaxation spectrum for PLA not aged and degraded during 120 min samples. In **Table 3** calculated values of G_i and λ_i are compiled. The chain scissions and the decrease in the molecular weight of the polymer after 120 min of thermo-oxidative degradation were confirmed by the lower relaxation times. Finally, also from this study, the plasticizing effect of Gly-POSS on the behavior of not-aged PLA was observed, the enhanced mobility of PLA chains reflecting in the lower relaxation times as compared with PLA or HO-POSS PLA. The shorter relaxation time observed for neat PLA and Gly-POSS PLA degraded during 120 min, indicating the presence of the larger amount of the short PLA chains facilitating the relaxation of the molt.

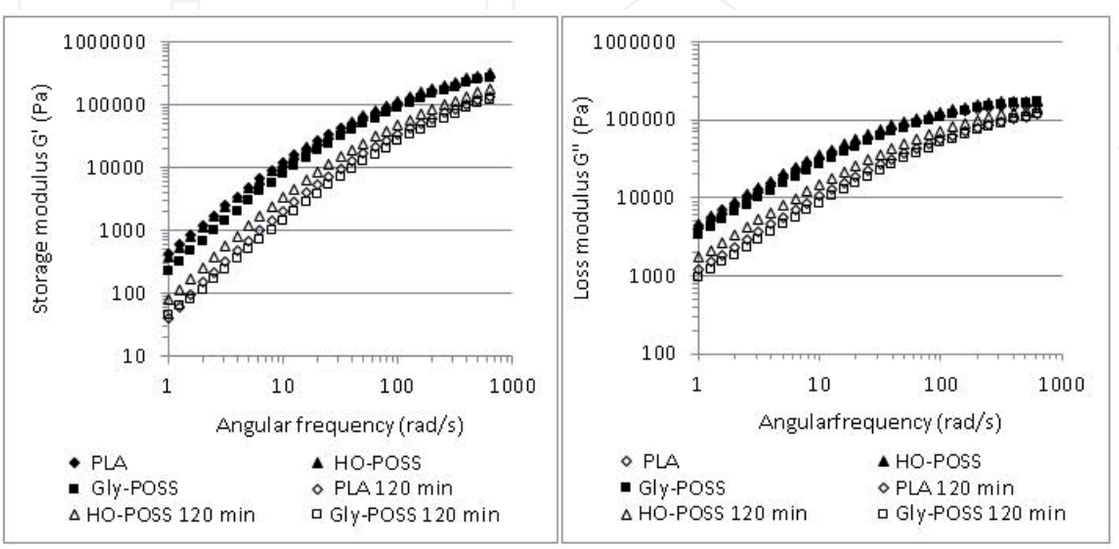


Figure 11.
Influence of the thermo-oxidative aging (120 min) on the viscoelastic properties (storage modulus G′, loss modulus G″) as a function of angular frequency ω for the POSS-modified PLA at 180°C.

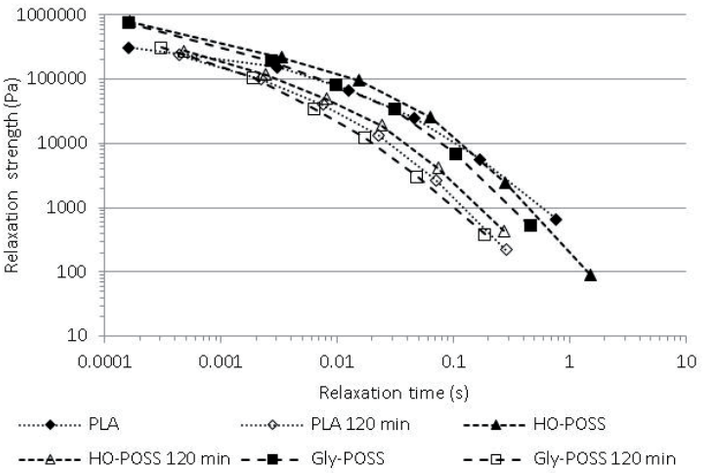


Figure 12.
Discrete relaxation spectrum for not aged and aged during 120 min PLA samples.

$R^2 = 0.9998$		Before aging		Time of aging 120 min	
Sample	**n**	**G_ikPa**	**λ_is**	**G_ikPa**	**λ_is**
PLA	1	308.888	$1.59 \cdot 10^{-4}$	235.202	$4.35 \cdot 10^{-4}$
	2	153.685	$3.06 \cdot 10^{-3}$	98.838	$2.23 \cdot 10^{-3}$
	3	67.539	0.01265	40.131	$7.53 \cdot 10^{-3}$
	4	24.786	0.04587	13.449	0.02266
	5	5.710	0.17028	2.662	0.07096
	6	0.665	0.76539	0.220	0.28426
PLA HO-POSS	1	783.398	$1.66 \cdot 10^{-4}$	275.002	$4.81 \cdot 10^{-4}$
	2	218.508	$3.31 \cdot 10^{-3}$	118.889	$2.45 \cdot 10^{-3}$
	3	95.374	0.01555	49.410	$8.13 \cdot 10^{-3}$
	4	25.367	0.06399	19.076	0.02409
	5	2.440	0.28063	4.138	0.07430
	6	0.090	1.50808	0.438	0.27293
PLA Gly-POSS	1	753.776	$1.59 \cdot 10^{-4}$	310.597	$3.06 \cdot 10^{-4}$
	2	191.331	$2.71 \cdot 10^{-3}$	106.000	$1.89 \cdot 10^{-3}$
	3	80.970	$9.87 \cdot 10^{-3}$	35.012	$6.27 \cdot 10^{-3}$
	4	33.950	0.03092	12.362	0.017141
	5	7.009	0.10387	3.062	0.04833
	6	0.521	0.46087	0.386	0.18548

Table 3.
The calculated values of relaxation strength G_i and relaxation time.

7. Conclusions

ENR/PLA composites were prepared by melt blending method. All prepared ENR/PLA composites showed immiscible droplet microstructure. The amount of added rubber strongly influenced on the tensile strength and elongation at break of blends. Incorporation of HO-POSS led to more homogenous morphology of

the blend resulting in the enhancement of tensile strength as compared with 50 ENR/PLA blend. Both incorporated POSS molecules influenced on the dynamic performance of the 50 ENR/PLA blend, decreasing the values of the storage shear modulus. The effect was attributed to the lubricating influence of the liquid POSS molecules. The amorphous structure of the 50 ENR/PLA blend modified by Gly-POSS accelerated the degradation of the material in soil as compared to neat 50 ENR/PLA blend and HO-POSS-modified blend. The cold crystallization of the blend was affected by the presence of rubber phase, the degree of crystallinity meaningfully decreased after the addition of the higher rubber ratio. Dynamic oscillatory measurements in melt state indicated that an increase of the melt viscosity and the storage shear modulus occurred during thermo-oxidative degradation at various degradation times for ENR/PLA blends resulting from curing reactions. Significant increase of the storage modulus G′ during thermo-oxidative degradation of the 50 ENR/PLA blend modified by Gly-POSS was observed. The HO-POSS enhanced the thermal stability of blend resulted in lower changes of both modulus and melt viscosity values after thermo-oxidative degradation. Similar stabilizing effect of HO-POSS was observed for virgin PLA; the thermo-oxidative degradation of the melt and chain scissions occurred in the lower extent after the incorporation of HO-POSS. Considering that one of the disadvantages of PLA is its thermo-oxidative and thermomechanical degradation during processing at higher temperature, the enhanced thermo-oxidative stability after incorporation of HO-POSS is promising.

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