ORIGINAL PAPER

Quantifying compositional and physical properties of antimicrobial polyethylene food packaging films using natural and sustainable fillers and additives

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ABSTRACT

In this study, LDPE compounds were prepared using different types of solid and liquid natural additives by melt compounding method. Spent coffee ground (SCG) and organoclay (OCL) powders were used as bio-based and mineral-based solid additives, respectively. Carvacrol and *Liquidambar orientalis* (LO) oil were used as functional liquid additives. Morphological, thermal, mechanical, viscoelastic, and antimicrobial properties of samples were characterized with various analytical methods and effect of solid and liquid additive combinations on the physical properties of film samples were quantified. It was observed that the SCG and LO oil made the film color darker but still transparent. Contact angle measurements indicated that the liquid additives increased the hydrophilicity of LDPE films. Based on the thermal and physical tests, it was found that the solid additives acted as reinforcing agents in LDPE matrix but liquid additives significantly modified the physical properties of LDPE composite films such as increasing the elongation and recovery rates and decreasing the creep strength as well as the improving the antimicrobial properties. Analyses the antimicrobial properties of samples using gram-positive and gram-negative bacteria exhibited that the carvacrol and LO oil significantly inhibited the bacterial growth. This study showed that transparent and antimicrobial flexible packaging films with thermal and mechanical durability could be prepared using sustainable, natural, and waste materials.

Keywords: Polyethylene; sustainability; antimicrobial film; food packaging.

INTRODUCTION

Food packaging has been historically considered as a defensive barrier that postpones the environmental impacts on foods. It has been reported that approximately 30% of population in developed countries are exposed to food-borne illnesses each year [1, 2]. Packaging is an effective way for extending the shelf life of foods and preventing microorganism contamination. One of the recent trends in food packaging

applications is introducing some functional compounds into the packaging materials or systems to improve the efficiency of various packaging functions. Antimicrobial food packaging is a concept of smart or active packaging approaches for inhibiting or preventing the growth of microorganisms, such as bacteria, fungi, and molds, on the surface of food products. Properly introducing several antimicrobial compounds into packaging materials could provide the following properties; (i) inhibition of bacterial growth on food surfaces, (ii) then extending the shelf life, and (iii) maintaining the textural property and taste consistency of food, in application [3]. Furthermore, antimicrobial packaging has been attracted more interests in active packaging applications as a result of growing trends in consuming minimally processed foods and raising awareness in the use of chemical additives, specifically preservative compounds in foods [4].

In recent years, preparation of functional, specifically antimicrobial, polyethylene films by blending or coating film surfaces with natural additives have been attracted much interests due to sustainability concerns [5-9]. This approach is a different way from the conventional additive-based formulation methods using inorganic antimicrobial agents such as silver or zinc nanoparticles. The most extensively studied natural compounds exhibiting antioxidant, antimicrobial or antibacterial effects and are extracted from various plants and herbs such as oregano, garlic, parsley, sage, coriander, rosemary, lemongrass, cinnamon, and clove. It has been reported that carvacrol shows a good antibacterial effect against a number of pathogens like bacteria, yeast, and mold and can be used as a food preservative due to its antibacterial feature. Numerous studies have been published about the antimicrobial properties of carvacrol loaded polyethylene films against the microorganisms such as *E. coli, A. alternata* and *S. choleraesuis* [3, 10-12]. Tas et al. prepared antimicrobial packaging films by coating corona treated LDPE surfaces with carvacrol loaded halloysite through a Layer-by-Layer (LbL) assembly method. They reported that coated films reduced the viability of a food pathogen, Aeromonas hydrophila by 85% and the aerobic count on chicken meat surfaces by 48% [13]. Doyadi et al. developed a new antimicrobial LDPE films containing natural compounds extracted from onion and potato peels by ultrasound assisted method. They prepared antimicrobial films by immersing the plasma-treated LDPE films into the extract solutions for coating the film surfaces and to use in packaging chicken thighs. Chicken thigh samples were packaged with the antimicrobial film. They reported that the chicken thigh showed lower thiobarbituric acid value (0.09 mg MDA/kg sample), total volatile nitrogen (14.27 mg/100 g), and total viable count (4.05 log CFU/g) compared to the control sample (pristine film) during 6 day-storage period [14].

It could be assumed that the important aspects for the utilization of natural functional compounds into packaging plastics are; (i) thermal stability of natural additives in polymer processing conditions, (ii) their compatibility with polymer matrix, and (iii) durability and/or stability for a long time as well as their performances in real application conditions. Therefore, selection of natural functional additive in particular

applications of industrial polymers and their proper adaptation to commercial polymer processing operations are highly challenging issues [11].

In this study, various natural additives and fillers were compounded with a commercial film grade LDPE and film samples were produced by melt processing techniques. Two solid fillers, spend coffee ground (SCG) powder and organoclay, and two liquid organic compounds, carvacrol and *Liquidambar orientalis* oil, as functional additives were used. Structural, morphological, thermal, mechanical, and antimicrobial properties of films were quantified depending on the filler type in the composition. *Liquidambar orientalis* oil as a natural bio-based functional additive was used in polyethylene films for the first time. *Liquidambar orientalis* oil is the extracted product obtained from one of the endemic trees of Turkey, Anatolian sweetgum tree (Liquidambar orientalis Miller), exists in south west part of Turkey Mugla, Marmaris, Fethiye, Koycegiz, Dalaman and Ula districts. Antimicrobial activity of *Liquidambar orientalis* oil against various pathogens such as *E. coli, S. aureus, C. albicans, B. suptilis, P. aeruginosa* and antifungal activity of essential oil of L. orientalis against *Phytophthora cactorum, Cryphonectria parasitica, and Fusarium circinatum* have been reported [15-18]. Plasticizer effect of *Liquidambar orientalis* oil has been recently showed [19].

EXPERIMENTAL

Materials

A film grade low density polyethylene (LDPE, Lupolen 2426H, LyondellBasell) with a density of 0.924 g/cm^3 and MFI value of 1.90 g/10 min. (ASTM D1238) was used as polymer matrix. Antimicrobial additives can be classified as solid lignocellulosic wastes as; (i) spent coffee ground powder and (ii) organoclay and liquid active components as; (iii) carvacrol and (iv) *Liquidambar orientalis* oil. Maleic anhydride grafted polyethylene (PE-g-MA, PolybondTM 3009) with a density of 0.950 g/cm^3, MFI value of 5.0 g/10 min. (ASTM D1238), and maleic anhydride graft ratio of 0.8-1.2 wt.% was used as compatibilizer.

Spent coffee ground was obtained from a local cafe as waste material and dried in an oven at 105°C for a day then grinded with a high-speed grinder and sieved. A particle size of 150-250 μm was used as filler. Organoclay was a commercial grade nanofiller (Cloisite® 15A, Southern Clay Products, USA), montmorillonite modified with a quaternary ammonium salt, hydrogenated tallow. The organic group content and density values of Cloisite® 15A were reported as 43 wt.% and 1.66 g/cm^3, respectively.

Carvacrol was obtained from the Indukern (Spain) with the purity of 0.99 and used as received. The *Liquidambar orientalis* (LO) oil was obtained from a local producer in Mugla, Turkey. Chemical composition of LO oil was characterized with a headspace gas chromatography-mass spectrometry

(GC/MS, Thermo Trace DSQ equipped with ZB5 MS column) analysis and reported previously [19]. In this reference, GC/MS spectrum of LO oil was given as Supplementary Information (SI). It was reported that the main components of LO were styrene (Retention time of 6.70 and CAS# of 100-42-5), α-methylstyrene (Retention time of 60.74 and CAS# of 98-83-9) and cinnamyl cinnamate (Retention time of 65.22 and CAS# of 122-69-0). The GC-MS results of LO oil were quantified and confirmed with the spectra of components using the NIST Chemistry WebBook, SRD 69. Detailed information about the chemical composition of LO oil can be found in Ref. [19].

Physical appearances of additives are given in Figure 1.

Staphylococcus aureus (*S. aureus*, ATCC6538) and *Escherichia coli* (*E. coli*, ATCC25922) were obtained from a local company.

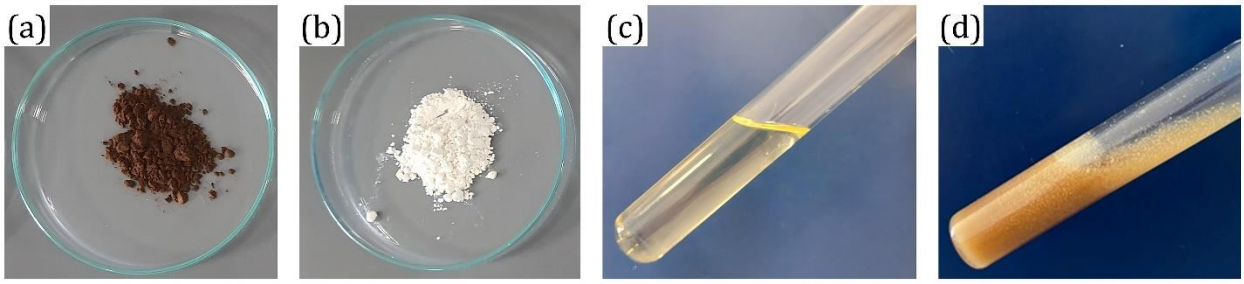

Figure 1. Physical appearences of solid and liquid additives (a) SCG powder, (b) OCL, (c) carvacrol, and (d) LO oil.

Sample preparation

Samples were prepared by melt blending method in an internal mixer (KokBir, RTX-M40, Turkey) operated at 75 rpm. The LDPE and compatibilizer were blended at 160 °C for 5 min. Then, functional additives were loaded into the device and compounded for 5 min. Sample notations and compositions are defined in Table 1. Film samples and dog-bone test specimens were prepared with compression molding method in a hot press (Qualitest, USA) by applying pressure of 50 bar at 150 °C for 3 minutes then the mold was quickly transferred to cold press and cooled under the same pressure with a cooling rate of 40/min.

Structural, thermal and physical characterization studies

Microstructural features of samples were characterized with a scanning electron microscope (Thermoscientific, Quattro S model SEM). Cross-sectional morphologies of samples, cryofractured in liquid nitrogen and then vacuum sputtering with a thin layer of gold, were analyzed in the SEM operated at 10 kV and different magnifications.

Thermal properties of samples were characterized with a differential scanning calorimeter (SII Nanotechnology, ExStar DSC 6200, Hitachi, Japan). Temperature and enthalpy calibration of the

instrument were carried out with the calibration standards of devices (In, Zn and Sn). In DSC analysis, 7-8 mg of samples were heated from 0 °C to 200 °C with a heating rate of 10 °C/min. and kept at this temperature for 5 min. then cooled to 0 °C with a cooling rate of 10 °C/min. The crystallized samples were heated up again from 0 °C to 200 °C with the same heating rate. All heating-cooling runs were performed under nitrogen gas with a flow rate of 50 mL/min. Degree of crystallization (X_c, %) values of samples were determined with the following equation;

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^{\circ}(1-\alpha)} \times 100 \quad (1)$$

where X_c is the degree of crystallization, ΔH_m is the melting enthalpy value of sample (J/g) experimentally determined from the second heating endotherm, ΔH_m^o is the melting enthalpy of 100% crystalline polyethylene (293 J/g), and (1-α) is the weight fraction of polyethylene in the specimen [3].

Solid state viscoelastic properties of samples were characterized by creep tests performed with a dynamic mechanical analyzer (SII Nanotechnology, ExStar DMA 6100, Hitachi, Japan) at 25°C. Creep tests of film samples were performed by loading an instantaneous stress of 5 MPa in uniaxial tension mode and monitoring time-dependent strain for 30 minutes.

Mechanical properties of samples were determined with tensile tests and carried out in a universal tensile test machine (Jinan Testing Equipment, WDW-20) with a crosshead speed of 20 mm/min according to the ISO 527-5A at ambient conditions. Tensile tests were performed with five specimens for each composition and the mechanical parameters were reported as average value and standard deviations. Representative photographs of tensile test specimens of samples are seen in Figure 2.

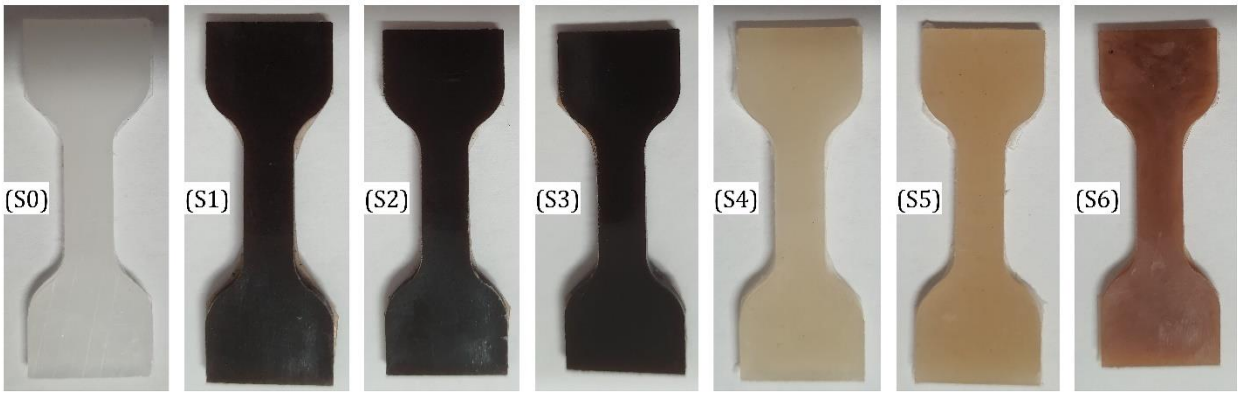

Figure 2. Representetive photographs of tensile test specimens.

Contant angle measurements were performed with Krüss FM41 contact angle measuring device equipped with a camera. In these measurements, 3-5 µL of distilled water was dropped on the surfaces of films at room temperature and the images of droplet were monitored with a camera and contact angles were determined with the software. Five measurements were done for each sample and the average values were reported.

Antimicrobial properties

Antimicrobial activities of samples were determined by the inhibition zone method (disk diffusion method). *S. aureus* and *E. coli* bacteria, taken from stock cultures and transported to the laboratory under cold storage conditions, were activated in a Tryptic Soy Broth (TSB) by incubating at 37 °C for 24 h. 0.1 mL of each inoculum was planted using the smear plate method on petri dishes containing Mueller-Hinton agar. Samples with a diameter of 10 mm were cut from the prepared films and placed in planted petri dishes. Control petri dishes without samples were prepared under the same conditions. All petri dishes were incubated at 37°C for 24 h. After the incubation, the petri dishes were checked for bacterial growth, and the inhibition zones around the films were evaluated qualitatively and quantitatively. Quantitative evaluation was made by determination of inhibition zone diameter. The zones seen around the films were interpreted as an indicator of the inhibition effect against bacterial growth.

RESULTS AND DISCUSSION

Morphological properties

Figure 3 represents the compression molded films and compares the transparency of samples, qualitatively. It is a well-known fact that the transparency is one of the most important physical features for flexible packaging films [20]. It is seen that all films yield almost the same transparency with the unfilled LDPE (S0). It was also found that the samples compounded with SCG powder (S1, S2, and S3) exhibited a slightly dark and brownish color and clearly seen particle agglomeration compared to those of OC samples.

Figure 3. Transparency of films.

The transparency and color of S4 and S5 samples are similar to the unfilled polyethylene film. It is seen that the S6 film is highly transparent but a little bit darker than the S5 and S5 due to the color of *Liquidambar orientalis* oil. Since these samples contain nanoscale filler and also compatibilizer, there is no visible filler agglomeration as seen in the S1, S2, and S3. It was observed that the transparency of S5 and S6 films was quite good. This could be attributed to the fact that the addition of liquid organic additives into the compound formulation improves the dispersion of clay layers in the polymer matrix.

Figure 4 shows the SEM images of solid fillers. The sizes of the OCL and SCG particles are also scaled on the figures. It is seen that an OCL particle is composed of many nano-thick and transparent layers and these layer agglomerates form particles with a size of 10-15 micrometers. On the other hand, SCG particles exhibit a characteristic lignocellulosic material morphology and much wider size distribution.

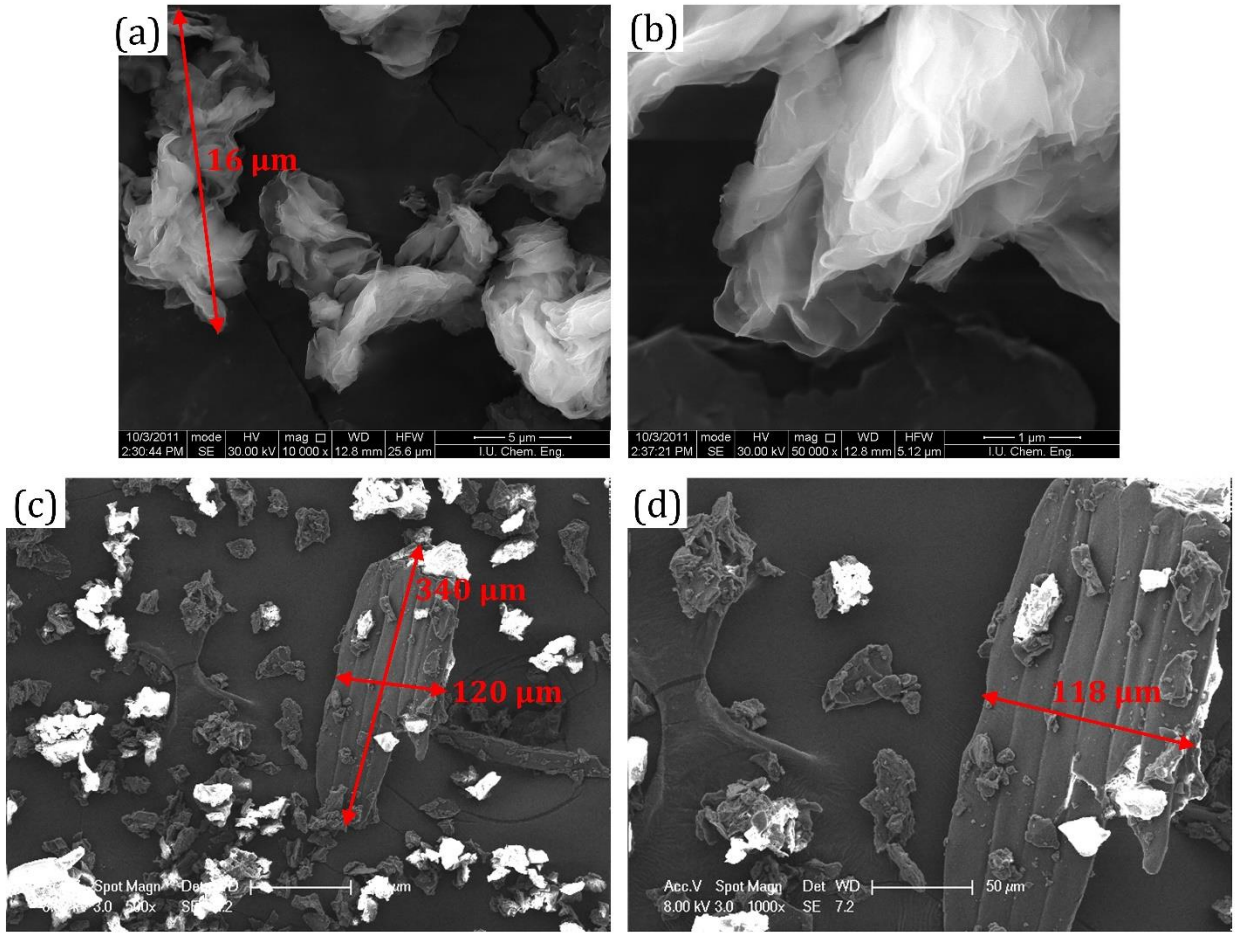

Figure 4. SEM images of solid additives; (a) and (b) organo-clay (OCL), (c) and (d) spend coffee ground (SCG) powder.

Figure 5 shows the SEM images of S1 and S4 samples at different magnifications. In the SEM images of S1 sample, it is seen that the filler-polymer interfacial interaction is excellent, especially in the

magnification of 20K. A SCG fiber with a diameter of 10 micron shows very strong adhesion with the polymer matrix and no voids are formed at the filler-polymer interface. Despite the excellent interfacial adhesion, it was observed that the distribution of SCG particles through the matrix was not homogeneous possibly due to very broad particles size distribution of SCG powder. In the SEM images of S4, it is seen that the clay layers are homogeneously distributed through the polymer matrix and no filler agglomeration is observed. Good filler distribution and excellent interfacial interaction observed in both samples imply the contribution of compatibilizer to the microstructure formation.

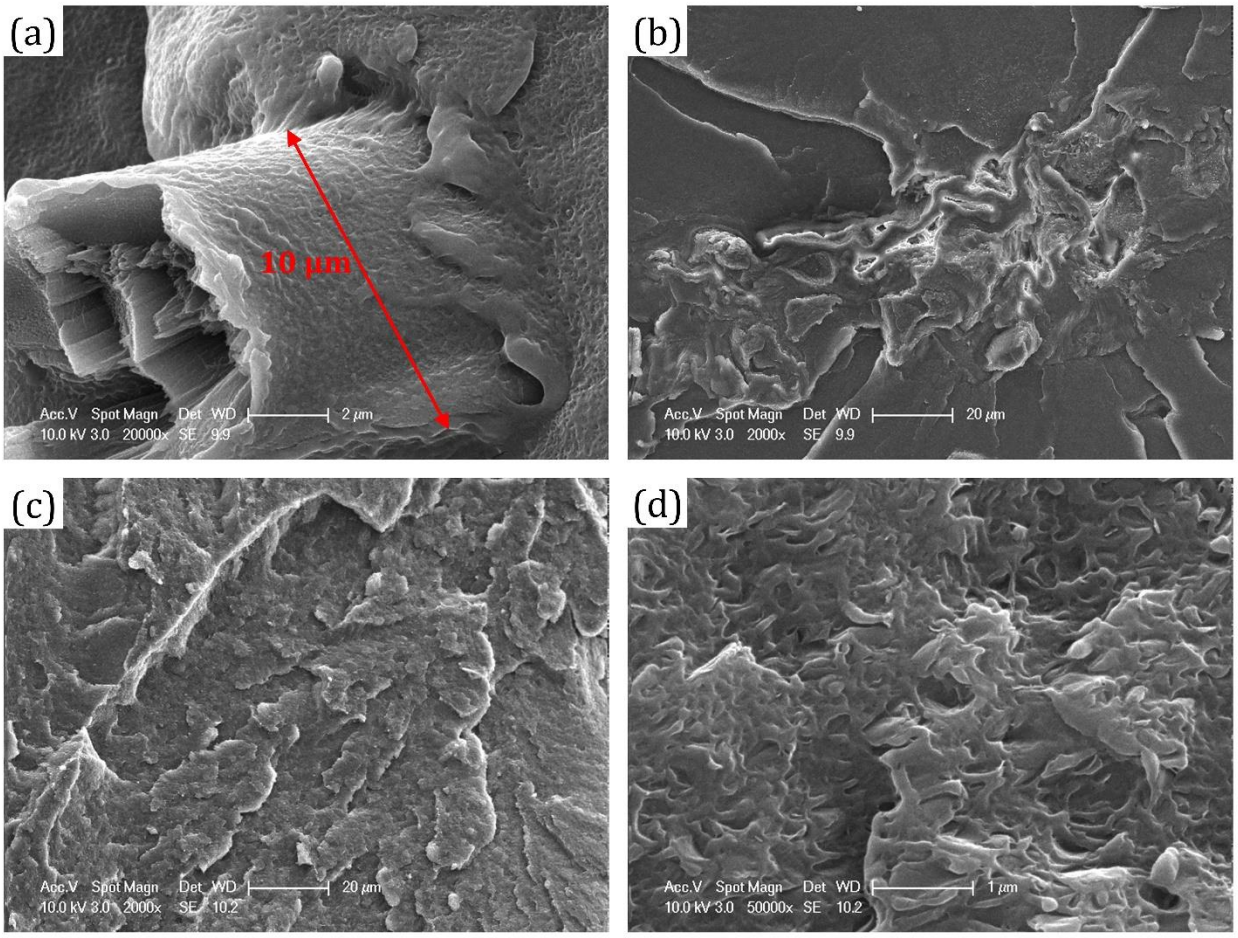

Figure 5. SEM images of samples, (a) and (b) S1, (c) and (d) S4.

Contact angle measurements

The contact angle of water is one of the main wetting properties of packaging materials and shows the hydrophilic/hydrophobic properties of the material [21]. It is a well-known fact that the contact angle values of polymer films are related to their polarity, surface energy, adhesive or cohesive forces and physical interactions with other solid or liquid materials. Figure 6 reports the contact angle values of samples.

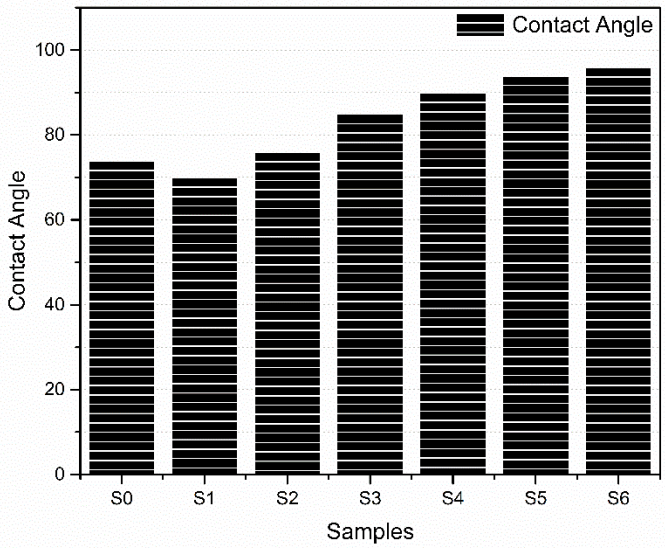

Figure 6. Contact angle values of samples.

It was found that the contact angle value of LDPE slightly decreased with the coffee powder addition while it increased with the organoclay addition. These results could be originated from the different characteristics of SCG and OCL powders. SCG is a hydrophilic lignocellulosic filler but OCL is an organically modified and organophilic filler. Rezaei et al. reported that the Cloisite®15A addition significantly increased the hydrophobicity and contact angle value of polyvinylideneflouride (PVDF)/organoclay mixed matrix membranes (MMMs). They also concluded that higher wetting resistance can be achieved with a good dispersion of organoclay particles in the polymer matrix [22]. Carvacrol and *Liquidambar orientalis* oil addition resulted in extra increase in the contact angle values of LDPE/SCG and LDPE/OCL composites. In other words, it means that the contact angle values of S2 and S3 were higher than S1 and similarly, the contact angle values of S5 and S6 were higher than S4 as seen in Figure 6. This finding can be expected by considering the organophilic natures of both liquid additives, carvacrol and *Liquidambar orientalis* oil. Sharma et al. reported that the thyme oil and clove oil addition increased the hydrophobicity and contact angle value of poly (lactide)-poly (butylene adipate-co-terephthalate) (PLA-PBAT) film [23].

Thermal properties of samples

DSC thermograms of samples are given as supplementary information in SI-1 and SI-2. The thermal parameters calculated from the DSC thermograms are listed in Table 2. It is seen in the DSC thermograms that all samples exhibit crystallization and melting peaks in a wide temperature range which is a typical behavior of LDPE due to highly branched chain structure. It is also observed that the crystallization peaks

show a small second exotherm in the temperature range of 60-65 °C. It was probably due to the contribution of long chain branches to chain ordering in lamellar structures as a secondary crystallization.

It was found that the addition of SCG (S1) and OCL (S4) increased the crystallization peak onset and peak maximum temperatures, and crystallization enthalpy values of LDPE possibly due to the nucleation effects of solid additives. It was obtained that the liquid component addition into LDPE/OCL and LDPE/SCG composites did not significantly affect the crystallization temperatures. Melting temperature of samples did not change depending on the composition. This result is consistent with the findings of similar compositions reported in the literature, previously. Zhang et al., and Persico et al. investigated the thermal properties LDPE/organoclay nanocomposites and concluded that there was no change in the melting temperature [24, 25]. Efrati et al. reported that essential oils did not affect crystallization temperature (T_c) of LDPE in composites prepared with LDPE, nanoclay, and oregano oil [2]. Degree of crystallization (X_c) values of specimens implied that the SCG and OCL addition slightly increased the X_c value of LDPE. The highest increase (about 5%) in X_c was observed in the S2 sample. This result could be attributed to the fact that carvacrol might act as an interfacial agent between polymer matrix and lignocellulosic filler.

Mechanical properties of samples

Figure 7 compares the mechanical property parameters obtained from the tensile test results of samples.

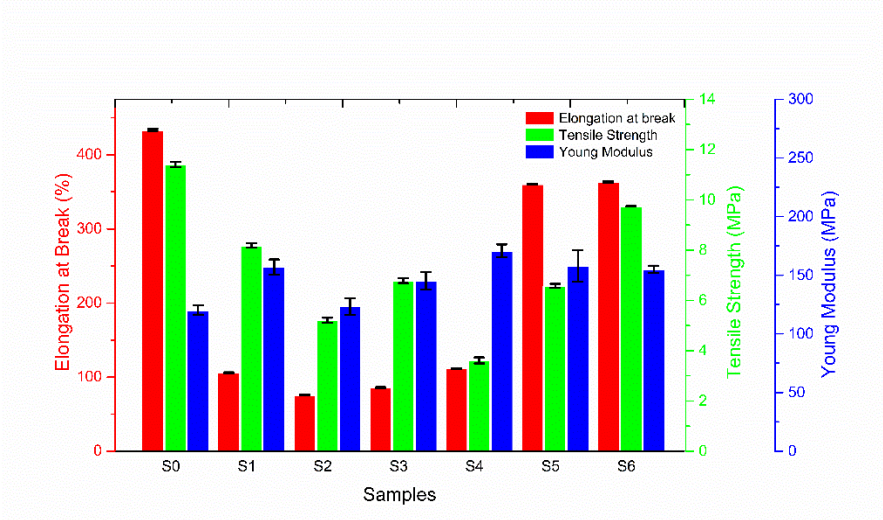

Figure 7. Mechanical properties of samples.

It was found that the addition of SCG (S1) and OCL (S4) improved the Young's modulus of LDPE as a result of reinforcing effect of solid fillers, as expected. This improvement was more pronounced for the 5 wt.% of OCL addition than the SCG due to its nano structure. Addition of 5 wt.% of SCG and OCL

significantly decreased the elongation at break value of LDPE. Similarly, filler addition slightly decreased the tensile strength of LDPE. Decrease in tensile strength in S1 was lower than S4. This result is probably due to the better interfacial interaction as mentioned before and seen in the SEM images of SCG loaded sample. These results are consistent with the previously reported findings. Leow et al. reported that the addition of SCG fillers acted as interfacial defects in composites and reduced the tensile strength [26]. Introducing liquid functional additives into the LDPE/SCG (S1) and LDPE/OCL (S4) samples did not dramatically change the Young's moduli of composite films but yielded different effects on the tensile strength and elongation at break values. Carvacrol and *Liquidambar orientalis* oil slightly decreased the tensile strength and elongation at break values of S1 sample whereas these additives improved the tensile strength and elongation at break values of S4, significantly. It can be originated from the fact that the organic liquids contributed to formation of better interaction between polymer matrix and hydrophobic organoclay layers and might act as a plasticizer in the systems. A similar effect has been previously discussed in the literature. Coelho et al. pointed out that the addition of essential oil caused a plasticizing effect on the polymeric matrix and increased the elongation and ductility [10].

Viscoelastic properties by DMA

Solid state viscoelastic behaviors of LDPE films were characterized with creep tests in this study and quantified with two different mathematical approaches, namely Findley and Burger models. Creep and recovery plots of films are given in Figs. 8(a) and 8(b) for the series of samples prepared with SCG and OCL, respectively. It is seen that the experimental, 30-minute, creep strain values of SCG and SCG+liquid additive loaded films were lower than LDPE whereas the OCL+liquid additive loaded samples exhibit higher strain values than LDPE and OCL filled film. This finding would be originated from the differences in sample microstructures and interaction between liquid components and solid fillers. As mentioned in the SEM images, strong interfacial adhesion between polyethylene and SCG probably resulted in higher creep resistance and lower creep strain in LDPE/SCG film. Additional liquid component introducing slightly improved the creep resistance due to the good compatibility of SCG surfaces with the highly polar organic compounds. It was obtained that the OCL addition also reduced the creep strain of LDPE, as expected. On the other hand, polar organic compounds exhibited an adverse effect on the creep behavior of non-polar LDPE+OCL composite films. This effect was more pronounced with the addition of carvacrol which is a monoterpenoid phenol.

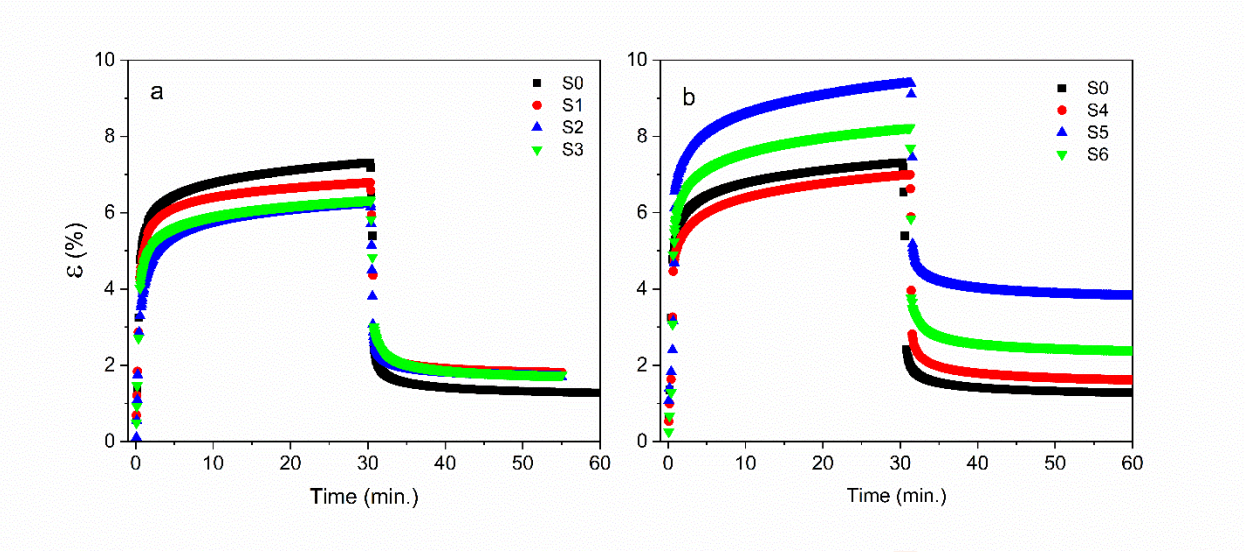

Figure 8. Creep and recovery plots of film samples prepared with (a) SCG and (b) OCL.

Another interesting result is the significant difference in recovery behaviors and permanent deformations of specimens. It is seen in Figure 8 that the SCG loaded samples exhibited almost the same permanent deformation and close to LDPE. But, the permanent deformation of OCL loaded films are higher significantly higher than LDPE after a 30 min. recovery period. Recovery percent (Rp, %) could be calculated by regarding the deformation values at 30 and 60 mins. The Rp value of LDPE was 82.5%. The Rp values of SCG loaded samples, S1, S2, and S2 were found to be 73.3%, 72.9%, and 72.6%, respectively. The OCL loaded samples, S4, S5, and S6 yielded the Rp values of 77.0%, 59.5%, and 70.7, respectively. These values implied that the solid fillers and liquid additives decreased the recovery percent of polyethylene which corresponded to higher permanent deformation under the stress of 5 MPa at room temperature.

$$\varepsilon(t) = \varepsilon_0 + A \cdot t^n \qquad (2)$$

where ε(t) is the total creep strain at time *t*, ε0 is the time-independent instantaneous elastic strain, A is the time-dependent strain, and *n* represents the time constant which is a stress-independent parameter stress-independent power-law constant or a material constant. It is known that the Findley parameters are mainly affected by the microstructural properties of polymers such as degree of crystallinity, entanglement or crosslinked density, level of physical interactions between polymer chains, applied stress, and test temperature. In filled system, creep behaviors of specimens also depend on the size and amount of filler, quality of filler dispersion, and polymer-filler interfacial interactions. In this study, it could be concluded

that the differentiation in creep behaviors of samples was originated from the compositional and microstructural variations because degree of crystallinity values of samples varied within 3-5 % depending on the filler and additive type as given in Table 2. As seen in Figure 9, Findley equation successfully fits the creep behaviors of samples. Findley model parameters are listed in Table 3.

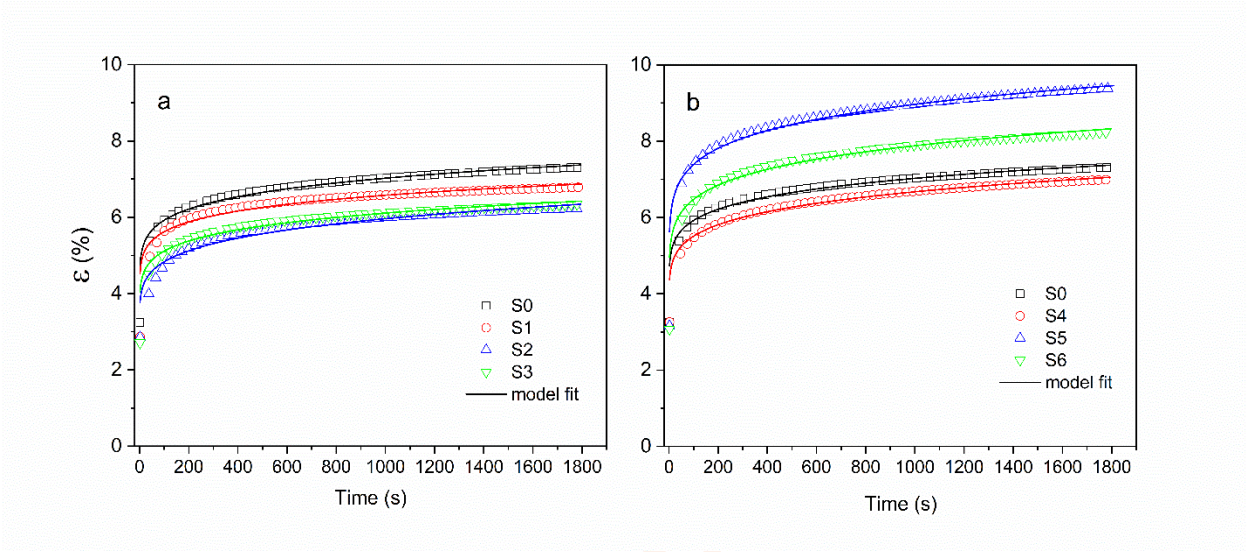

Figure 9. Findley model fit of creep curves of film samples prepared with (a) SCG and (b) OCL.

It was obtained that SGC loaded films reduced that instantaneous elastic strain (□0) of LDPE due to higher elastic modulus of these specimens than LDPE. The □0 values of OCL loaded specimens were found to be close to LDPE but liquid additives slightly decreased the □0 values in this series of samples while the ε_0 was not affected much with the liquid addition for the SCG loaded samples. The A values did not exhibit a correlation with the filler and additive type. But, the lower A values of S2 and S4 and the highest A value of S5 could be considered as interesting result compared to LDPE. The lower A value of S4 would correspond to the restriction effect of 2D clay nano layers on the mobility of polyethylene chains. On the contrarily, higher A values of S5 and S6 can be explained with the increase in chain mobility by liquid addition yielding higher creep strain compared to S4 and S0. It was found that the power-law index (n) of samples varied in the range of 0.13-0.20.

The four-parameter Burger model was also used to quantify the creep behaviors and viscoelastic properties of film samples [27]. Burger model is a simple combination of Maxwell and Kelvin–Voigt elements in linear viscoelasticity theory and mathematically defined as;

$$\varepsilon(t) = \frac{\sigma}{\Delta E_m} + \frac{\sigma}{E_K}\left[1 - exp(\frac{-E_K \cdot t}{\eta_K})\right] + \frac{\sigma \cdot t}{\eta_M} \qquad (3)$$

where σ is the applied stress (5 MPa, in this study), E_M and η_M are the elastic and viscous components of Maxwell element, and E_K and η_K are the elastic and viscous components of Kelvin element, respectively. In addition to these parameters, creep rate ($\acute{\varepsilon}=\sigma/\eta_M$, s^{-1}) and retardation time (τ) which is the ratio of η_K/E_K (s), can also be determined from the Burger analysis. A detailed explanation of Burger equation and physical meanings of model parameters can be found elsewhere [28-31]. The nonlinear curve fitting was performed by OriginPro 2018 software. Burger fits are illustrated in Figure 10 and the calculated model parameters are listed in Table 4.

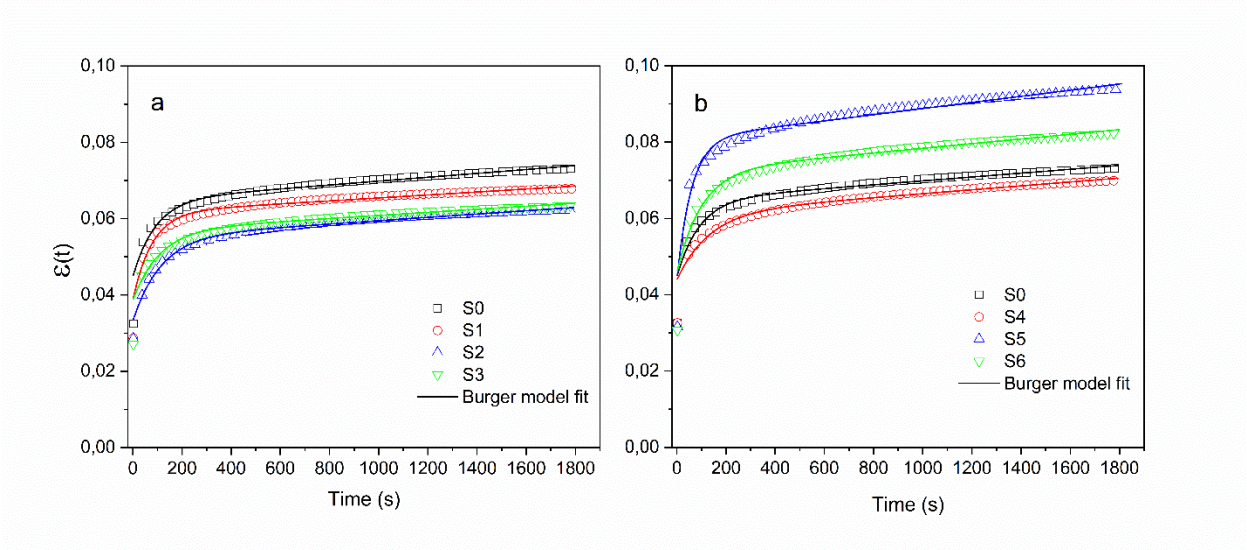

Figure 10. Burger model fit of creep curves of film samples prepared with (a) SCG and (b) OCL.

It is seen in Figure 10 that the Burger model successfully fits the creep behaviors of samples. The parameters EM and EK correspond to instantaneous and recoverable elasticity, in another word, the Young's modulus, and retardant elasticity of the system, respectively. It was found that the SCG addition improved the elasticity of LDPE This result is very consistent with the tensile test results mentioned before. The η_M can be considered as the analogous of zero-shear rate viscosity (η_0) parameter in rheological measurements. The addition of SCG and SCG+liquid additives into LDPE matrix significantly increased the η_M value of PE. This effect clearly implied the restriction effect of solid filler on the mobility of polymer chains. On the other hand, introducing liquid additives into the LDPE/OCL composite significantly reduced the η_M value. This result can be originated from the plasticization effect of carvacrol and Liquidambar orientalis oil for the LDPE/OCL system. The S4 sample yielded the highest retardation time and the S5 yielded the lowest retardation time. This finding allows us to recognize the different effects of solid fillers and liquid additives on the chain mobility and thus the viscoelastic behavior of system. It was found that

the SCG addition decreased the creep rate of LDPE. The highest creep rate was obtained for the S5 sample prepared with the OCL and carvacrol.

Antimicrobial properties

In antimicrobial performance tests, disc-shape samples with a diameter of 1 cm and a thickness of 2 mm were used in the gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria medium. Figure 11 compares the diameters of inhibition zones of samples as column graph and illustrates the representative photographs of two bacteria.

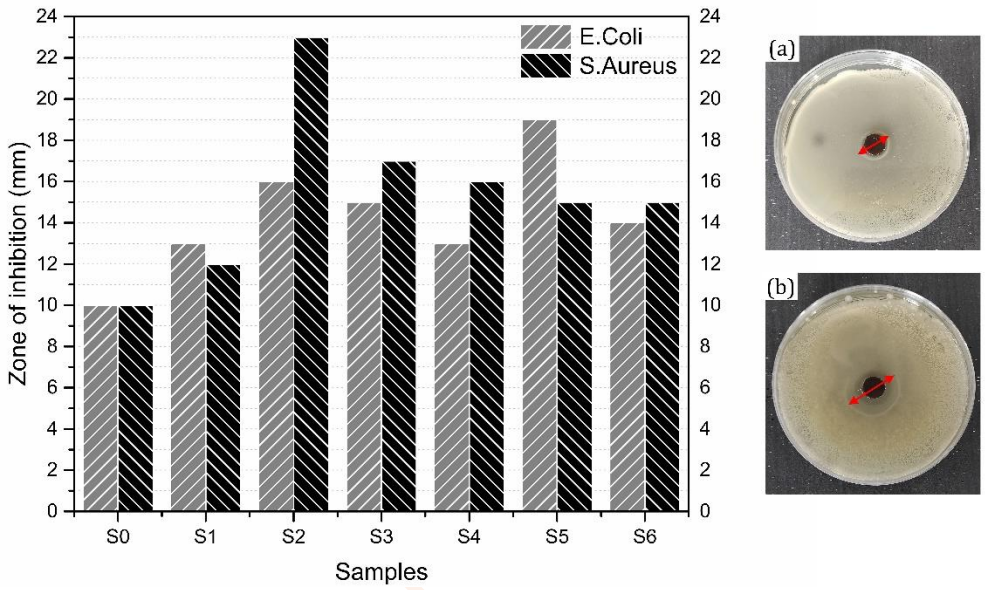

Figure 11. Antimicrobial results of samples (a) E.coli zone and (b) S. Aureus zone.

It can be concluded that similar results were obtained for gram-positive and gram-negative bacteria. Inhibition zones of SCG and OCL loaded samples were higher than LDPE. Carvacrol and *Liquidambar orientalis* addition into the LDPE/SCG sample increased the diameter od inhibition zone that corresponded to improvement in antimicrobial performance. On the other hand, carvacrol and *Liquidambar orientalis* oil addition into the LDPE/OCL sample increased the inhibition zone diameter for the gram negative bacteria and decreased for the gram positive bacteria. It has been concluded that the desorption or diffusion of liquid additives from polymer structure forms halo in the bacterial medium. This result indicates that microorganism growth can definitely be inhibited on the film surface. It can also be concluded that these films could also inhibit the growth of microorganisms in the case of long-term storage conditions. Similar results have been reported before about the superior antimicrobial effects of carvacrol and *Liquidambar orientalis* [18, 23, 32, 33]. Shemesh et al. designed nanoclays as carvacrol carriers and reported that

LDPE/(clay/carvacrol) nanocomposites exhibited excellent and long-term antimicrobial activity against *E. coli* bacteria while LDPE/carvacrol films lost their antimicrobial function within a few days [34]. Efrati et al. tested antimicrobial properties of different polymeric films loaded with nanoclays and thymol against *E. coli*. a common foodborne bacterial pathogen [2]. They reported that the migration of thymol throughout the film sample was significantly affected by the crystallinity of polyethylene [2]. Shemesh et al. examined LDPE composites including carvacrol as antimicrobial agent encapsulated by halloysite nanotubes (HNTs) and reported that these composites showed excellent and extended antibacterial properties against *E. coli* and *L. innocua* [3]. Lopez et al. stated that thyme oil exhibited antimicrobial effect for the polypropylene (PP) [35]. Krepker et al. reported excellent antimicrobial activity of LDPE/carvacrol films against *E. coli* and *A. alternata* and *Rhizopus spp.* by *in-vitro* micro atmosphere analysis [11]. Fatima et al. revealed that SCG extract showed antioxidant and antibacterial activity due to its diverse and rich chemical composition [36].

CONCLUSION

In this study, antimicrobial polyethylene films were prepared by introducing natural and robust solid and liquid fillers and additives into low density polyethylene (LDPE) matrix via melt compounding method. Morphological, mechanical, thermal, viscoelastic and antimicrobial properties of samples were characterized and structure-property relationships of films were quantified depending on the compositional variations. It was found that solid fillers improved the mechanical properties of films whereas liquid additives yielded a significant increase in creep rate. Antimicrobial performances of films revealed that microorganism growth was successfully inhibited on the film surfaces. It has been concluded that the antimicrobial LDPE films reinforced with natural, sustainable and functional additives can maintain their structural and physical properties for a long time and they could be considered as suitable and promising materials for food packaging applications.

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Table 1. Sample notations and compositions.

Samples	wt.(%)				(phr)	
	Polymer	Compatibilizer	Solid fillers		Liquid additives	
	LDPE	PE-g-MA	SCG	OCL	carvacrol	LO
S0	100					
S1	92.5	2.5	5			
S2	92.5	2.5	5		5	
S3	92.5	2.5	5			5
S4	92.5	2.5		5		
S5	92.5	2.5		5	5	
S6	92.5	2.5		5		5

SCG: spent coffee ground
OCL: organo-clay
LO: Liquidambar orientalis oil

Table 2. DSC parameters of samples.

Samples	T_c, onset (°C)	T_c, peak (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
S0	97.4	87.4	93.0	115.5	100	34.1
S1	101.5	92.6	100	113.7	100	35.9
S2	102.0	92.4	106	114.7	109	39.1
S3	101.4	91.5	103	114.3	100	35.9
S4	101.5	91.0	106	115.2	103	37.0
S5	101.3	92.0	104	115.1	102	36.6
S6	101.0	92.1	102	113.5	99	35.5

Table 3. Findley parameters of samples.

Samples	ε_0	A	*n*	R^2
S0	3.24	1.35	0.15	0.964
S1	2.87	1.52	0.13	0.921
S2	2.86	0.80	0.20	0.939
S3	2.71	1.20	0.15	0.955
S4	3.26	0.98	0.18	0.979
S5	3.16	2.25	0.14	0.952
S6	3.07	1.70	0.15	0.959

Table 4. Burger parameters of samples.

Samples	E_M (MPa)	E_K (MPa)	η_M (MPa.s)	η_K (MPa.s)	τ (s)	$\dot{\varepsilon}$ ($x10^{-5}$, s^{-1})	R^2
S0	22.3	49.9	197450	4567	92	2.53	0.974
S1	25.9	43.6	257450	3380	78	1.94	0.975
S2	30.1	45.6	230160	5194	114	2.17	0.991
S3	25.9	54.8	249020	5880	107	2.00	0.977
S4	22.7	57.3	195650	7490	130	2.55	0.982
S5	22.8	27.1	124590	1600	59	4.01	0.964
S6	21.8	37.7	163910	3763	100	3.05	0.974