Regular Article

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LLDPE matrix with LDPE and UV stabilizer additive to evaluate the interface adhesion impact on the thermal and mechanical degradation

https://doi.org/10.1515/eng-2022-0429
received December 15, 2022; accepted March 13, 2023

Abstract: Linear low-density polyethylene (LLDPE) is a commodity material that has been increasingly used in various open environments owing to its versatile properties. The mechanical and thermal degradation and processability properties can be enhanced by blending with other polymers or using different types of fillers to adjust such properties to fit the required applications. The objective of this work is to investigate the polymer–polymer interface and compare it with the polymer–additive (microparticles) interface in terms of structural changes and the impact on the polymer environmental properties. The novelty of this work is how to control the adhesion at the interface to enhance selected properties of the polymer without compromising other properties. LLDPE dried resins were compounded with UV additive and different wt% content of LDPE resin separately in a twin-screw extruder at 180–200°C and 150 rpm rotating speed with a die head to produce 1 mm thickness sheets. Then the prepared specimens were cooled to ambient temperature for testing. The nuclear magnetic resonance results showed that LLDPE with microparticles has good phase adhesion compared to the blended samples with LDPE. Moreover, thermal gravimetric analysis showed that the blends decompose in two steps at high LDPE content. The morphological images revealed cavities in the microstructure of low weight percent blends inductive of the relatively weak interaction between the components. The present study conclusively demonstrates that the polymer matrix is more stable with microparticle fillers (UV stabilizer) additive than with LDPE, which impacts the environment durability for outdoor application.

Keywords: polymer matrix, microparticles, NMR

1 Introduction

Polyethylene (PE) or polythene is the most common plastic and has the highest share of global production [1]. It has wide usages in packaging, plastic bags, plastic films, geomembranes, bottles, etc. The most important polyethylene grades are low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE). LLDPE is currently a fast-growing polymer used in packaging. Globally, around 80% of LLDPE goes into film applications for food and non-food packaging, shrink/stretch film, and non-packaging uses [2–4]. LDPE has lower tensile strength and higher resilience than LLDPE. Moreover, it is less crystalline since its molecules are less tightly packed [5]. The trend in food packaging films is toward high-performance film structures that are less permeable to increase the shelf life and enhance the flavour. However, such desirable performance cannot be achieved with a single polymer. Therefore, many research activities were directed to select a blend of polymers or use additives for specific applications, including those for packaging and food packaging. A polymer blend is a mixture of two or more polymers that have been blended to create a new material with different physical properties [6,7]. There are three categories of polymer blends: immiscible polymer blends, compatible polymer blends, and miscible polymer blends [8]. These categories indirectly describe the behaviour of the polymers at the interface, which impacts the properties of the blends and is adjusted according to the usage by the correct selection of the component polymers [9]. In comparison, the use of special

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additives is also considered an attractive technique to produce enhanced polymeric materials with specific properties. Additives can impact polymer processing by four primary mechanisms – adsorption, abrasion, site competition, and chemical reaction. Light stabilizers, in particular, are growing faster than fillers and other additives at over 7% per year [10,11].

Consequently, it becomes mandatory to assess the efficiency of additives or blending with respect to the polymer matrix and the interface changes [12,13]. For example, polyethylene linear low-density blend with to alter certain properties such as improved mechanical and thermal properties. When blending, although the densities of LDPE and LLDPE (0.921–0.926 g/cc) are similar, LLDPE displays better tear and impact film properties than LDPE [14]. Therefore, adding LLDPE to LDPE is expected to improve thermal as well as good barrier properties. In producing polymers with desirable final properties, it is essential to study the interface adhesion; this demands characterizing and understanding the interfacial reaction under processing conditions. Such deviations critically determine the final physical properties of materials prepared from multicomponent macromolecules. In the literature, numerous articles can be found about the role of interfacial adhesion in altering the polymer properties [15–17]. To evade interfacial failure in the presence of filler and miscible blend, it is essential to ensure good adhesion properties at the interfaces. In the industry, the manufacturer needs to ensure that the composite parts are properly bonded together and that this bond will endure. Nuclear magnetic resonance (NMR) is an outstanding experimental tool to understand whether certain polymeric chains are miscible or phase separate and to define the final state of mixing in solid materials. The end-use physical properties depend on the state of mixing [18,19].

Understanding this structural change is crucial in material science to correlate structural parameters with the final properties of a material. This article focused on investigating the influence of the structural changes at the interface of different enhancement techniques for LLDPE outdoor application. Samples of LLDPE were blended with different contents of LDPE and UV stabilizer (as microparticles). The prepared samples were evaluated for structural changes, thermal stability, mechanical properties, and morphology.

2 Materials and methods

2.1 Samples collection

The LLDPE and LDPE were received from a local manufacturing company and Qapco. The material properties of each sample are given in Table 1. The stabilizer additive was UV additives (Tinuvin 494FB, Tinuvin NOR 371, and Chimasorb 81) acquired from "Aldrige" chemical company.

2.2 Sample preparation and testing

The polymer pellets were dried at 80°C in a hot air oven for blending. Then the materials were sealed in plastic bags and kept in desiccators prior to blending. The samples were compounded by simultaneously adding both components to the twin-screw extruder at the selected wt% content. During the compounding of all blends, the barrel temperature profiles varied from 180 to 200°C over the six zones at the rotating speed of 40 rpm (to allow more residence time for the blend). For UV additive, the masterbatch that contained LLDPE and UV additive was prepared in a mixer, and then compounded in a twin extruder at 180–200°C at a rotating speed of 150 rpm. All test samples were rested under ambient conditions for a period of 24 h.

Mechanical and thermal properties were tested according to ASTM D 638 and ASTM D 3850-200, respectively [20,21].

2.3 NMR

NMR 400 MHz was used under the solution technique in which the polymer is partially dissolved in acetone to

Table 1: Polymers material properties

Name	Grade	Melt flow index (g/10 min)	Density (g/cm^3)	Melting point (°C)	Haze (%)	Gloss (GU)
LDPE	FB3003	0.30	0.920	109	13	40
LLDPE	EFDC-7050	2.00	0.918	124	14	50

ensure the solution state so that NMR can detect it. The samples were ground and then mixed with acetone-d6. Proton one-degree NMR pulse sequence was applied for each sample separately (90-degree pulse sequence; proton is the name of the pulse in topspin; one-degree pulse sequence; duration time, 26 s; relaxation time, 2 s; power, 18.911 W; several scans, 100 scans). The NMR spectra were obtained for the samples and analysed using BRUKER software.

Morphological: Morphology of the samples was examined using a scanning electron microscope (SEM), a TESCAN TS5135MM model. The specimens were sputter-coated with a thin layer of gold by using vapour deposition techniques to avoid electrostatic charging during sample examination.

2.4 Thermogravimetric analysis (TGA)

TGA (TGA-50H from Japan, Shimadzu) was used under air at 40 mL/min flow rate. This test determines the changes in the sample weight with an increase in temperature, as the onset temperature is directly calculated from the TGA traces corresponding to the temperature at which the weight loss begins. The experimental temperatures varied from ambient temperature to 700°C with a heating rate of 10°C/min.

2.5 Statistical analysis

The experiments were conducted with five replicates per condition. The results were analysed statistically using the average of three techniques with less than 1% error in the final results for each condition.

3 Discussion of results

3.1 NMR

The research on the characterization of LLDPE and the prepared samples based on the H-NMR technique is scarce. However, the protons of the methylene (CH_2) and methyl (CH_3) chemical groups appear in separate chemical shifts in the H-NMR spectra, and thus H-NMR was used to characterize these chemical groups. Different categories of interfaces are examined systematically by NMR to isolate the role of the interface in the enhancement of different properties for a specific application [22]. This section discusses the separation and dynamic behaviour of the prepared samples.

Figure 1a and b shows that the blends were immiscible in the melt. Moreover, the peaks at 1.4–1.55 ppm were not observed in the case of 50/50% LLDPE/LDPE, which indicates the weak interfacial stability of the blend matrix. In the case of Figure 1b, at higher LLDPE content, the blend showed less chemical shifts indicating a better adhesion at the interface, this could be attributed to the high side branching nature of LDPE. The chemical shift is most often used for structure determination through the shield patterns. In Figure 1c, the chemical shield shift is almost negligible, indicating a strong bonding of the UV stabilizer microparticles at the interface without causing a restructuring of the lamella. Moreover, NMR analysis shows as in Table 2 a breakdown of the functional group at the interface of the LLDPE, which affects the phase stability of the blend.

Therefore, samples with microparticle additives showed more interfacial stability in the polymer matrix, keeping the lamella structure intact without changes; this will be reflected in the polymer properties. On the other hand, the behaviour at the LLDPE/LDPE blend interface was affected by the nature of the individual polymer, such as the weak intermolecular forces of LDPE and the considerable short branch LLDPE indicated by the chemical shield shift.

3.2 SEM

SEM was used to study the differences in morphological and interfacial properties between the two enhancement methods of LLDPE and to confirm the findings from NMR. The visual examination of the matrix through SEM was not practically very clear because the blend materials have almost the same density, which directly affects the contrast in SEM. The light colour (light grey and white) represents the contrast between the different phases. In Figure 2a, the blend of low content of LLDPE (20%) with LDPE demonstrates the worst adhesion of the whole sample. A clear white interface can be noticed, indicating detachment between the phases; thus, the light patches are predominantly due to compositional contrast. Furthermore, in Figure 2b, the low adhesion at the interface is also noticed with less amount due to the higher content of LLDPE (50%). This indicates that LDPE spherulites disappeared, and LDPE became the continuous phase. Moreover, the obtained morphology indicated the absence of

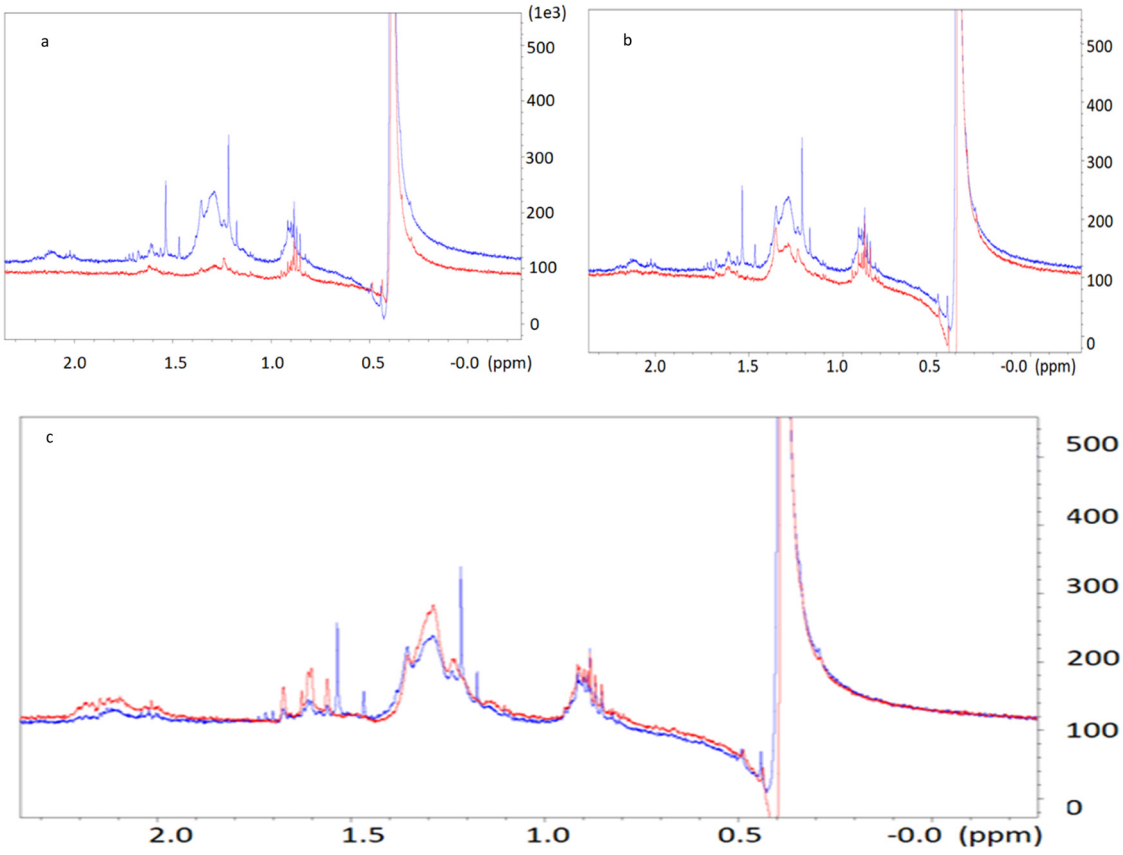

Figure 1: H-NMR spectra of LLDPE in blue: (a) 80/20 LDPE/LLDPE in red, (b) 50/50% LLDPE; LDPE in red, and (c) LLDPE with UV 0.3% in red.

miscibility between the two polymers. The surface morphology of the LLDPE sample with UV stabilizer microparticles is shown in Figure 2c. The micrograph shows the continuous phase of LLDPE with uniform distribution of the microparticles with no dark patches that represent structural changes due to particle agglomeration.

Table 2: NMR functional group peaks along with the interface for LLDPE

Peak	*v*(F1) (ppm)	Chemical molecule
1	2.131	CH_3COR
2	1.6101	CH
3	1.5358	CH
4	1.4672	CH
5	1.3555	CH_2
6	1.289	CH_2
7	1.2162	CH_2
8	1.1749	CH_2
9	0.9157	CH_3
10	0.8891	CH_3
11	0.8827	CH_3
12	0.8696	CH_3
13	0.8531	CH_3

In general, the micrograph image synergies with NMR results show the stability of the polymer matrix for LLDPE samples with microparticles and interfacial unsteadiness for the blend samples even for LLDPE 50% content.

3.3 Thermal stability

TGA was carried out for the prepared samples to investigate the thermal degradation of the prepared films. It is essential to realize that when a proper interface interaction exists, the particles can restrain/ease the movement of a polymer chain, making it less difficult to break the polymer chains occurring at a lower temperature. Therefore, the prepared blend showed an earlier degradation temperature than pure LLDPE.

TGA analysis of the prepared samples is provided in Figure 3. The thermogram suggests that the onset of degradation started around 240–250°C for most of the blend compositions. On the other hand, the temperature at maximum degradation commenced after 400°C. Once the temperature rises above 250°C, the epoxy resin starts to decompose rapidly. The single degradation step for the

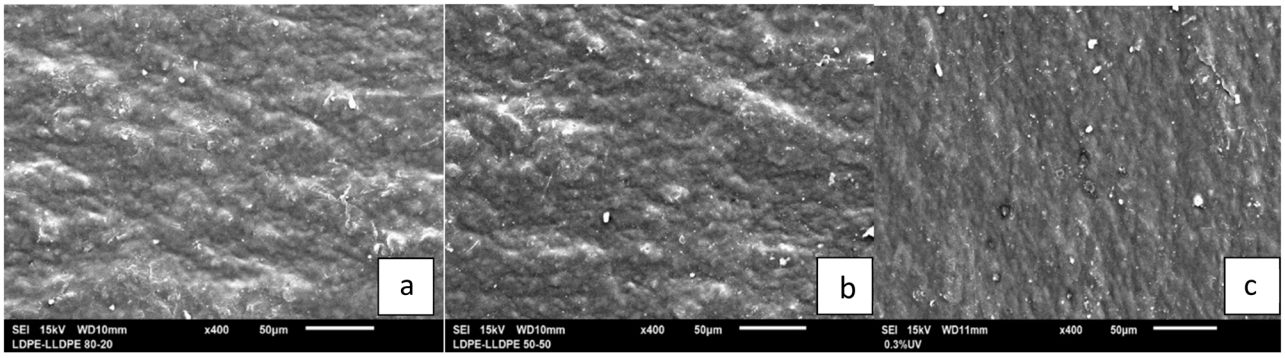

Figure 2: Surface morphology of (a) LDPE/LLDPE blend (80/20), (b) LDPE/LLDPE blend (50/50), and (c) LLDPE with UV stabilized microparticles.

polymer blend confirms the stability of the blend and that the polymers are composed of carbon–carbon bonds in the main chain, thereby allowing a temperature increase to promote random scission. Associated thermal degradation and thermal depolymerization occur at a weak part of the polymer's main chain [23,24]. Moreover, for LDPE in Figure 3a, a smooth degradation is noticed as it is a decomposition of pure material, wherein in Figure 3b it is noticed that

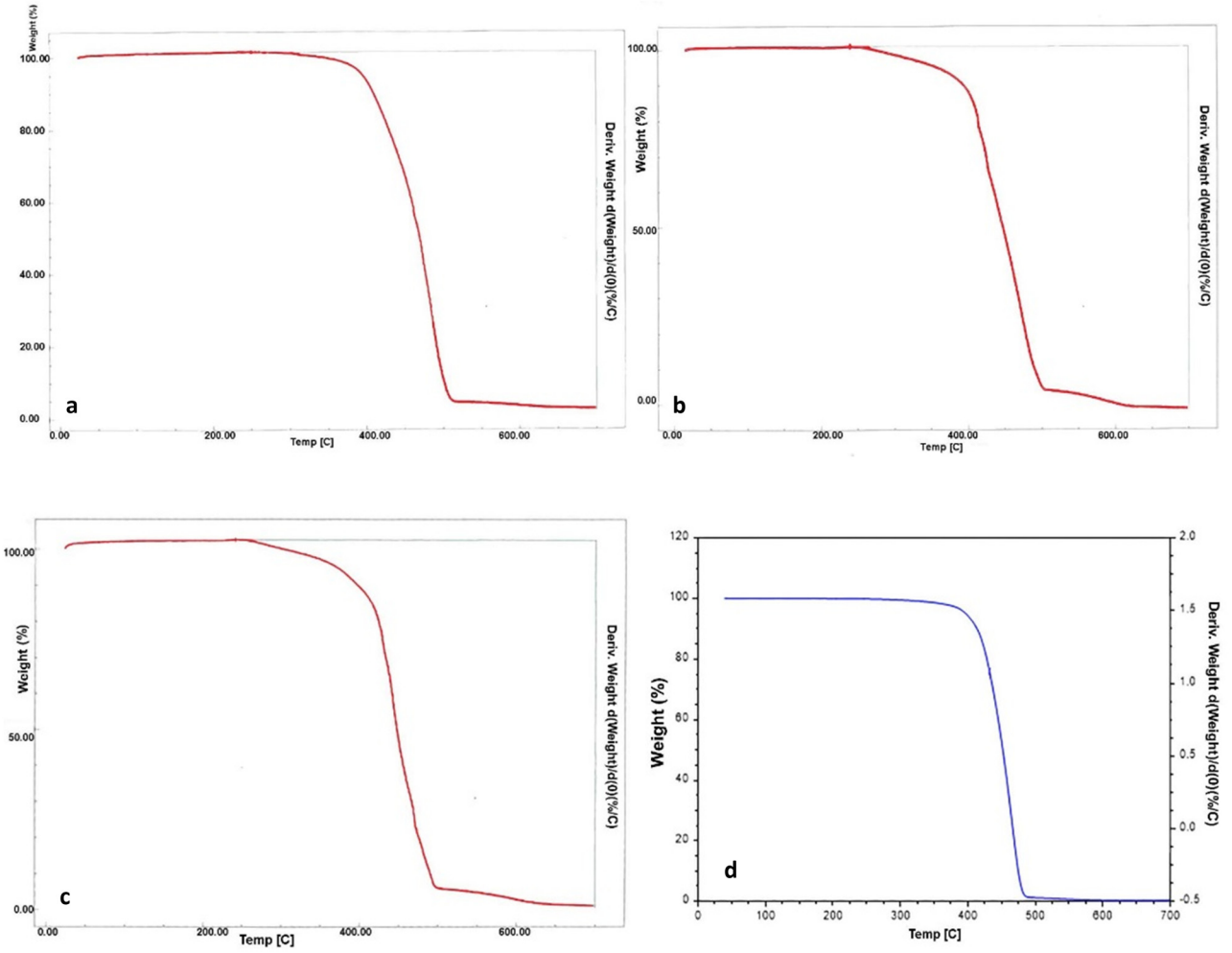

Figure 3: (a) TGA of LDPE pure, (b) TGA of 20/80 contents of LLDPE/LDPE blend, (c) TGA of 50/50 contents of LLDPE/LDPE blend, and (d) TGA of LLDPE with microparticles (UV stabilizer).

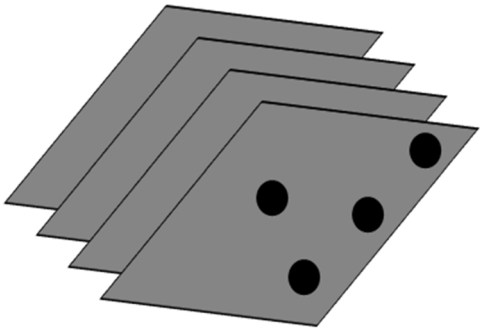

Figure 4: Expected distribution of microparticles in the lamella phase of LLDPE.

samples with high LDPE content of 80% experience an unstable double stage at 500°C before complete decomposition which can be attributed to the breaking of the chain due to the high concentration of the LDPE in the blend. However, in Figure 3c, at high LLDPE content (50%), the blends decompose in two steps, first slowly, then rapidly, as it reaches 400°C; this could be attributed to the incompatibility behaviour of the blend at high LLDPE content, which synergies with the results produced from the NMR and SEM.

In addition, there was a visible influence of the individual polymer components on the thermal stability of each blend, indicating that LLDPE dominated the structural changes at the interface.

For the samples with microparticles UV stabilizer Figure 3d, the delay in starting decomposition temperature for the high LLDPE content could be attributed to the decrease in the additional strength of the LLDPE interface and the UV stabilizer particles [25,26]. This forms distinct lamellae morphologies and thicknesses, the layers of the lamella are expected in the shape as shown in Figure 4. The smooth one-stage decomposition that started at 490°C indicates a thermally stable polymer matrix due to the uniform adhesion of the microparticles at the interface of the LLDPE.

3.4 Mechanical impact

The impact of the structural changes and the level of adhesion at the interface can always be detected by altering the mechanical properties of the composites. In

Table 3: Mechanical properties of the prepared samples

Sample	Elong. @ peak (mm)	Stress @ break (N/mm²)	Strain @ break (%)	Stress @ peak (N/mm²)
LDPE/LLDPE 100/0	138.3	16.7	282.8	19.1
LDPE/LLDPE 0/100	721	19	1481.2	19.4
UV/LLDPE 0.3%	498.3	21.7	951.4	29.1
LDPE/LLDPE 80/20	400.128	17.703	805.585	20.51
LDPE/LLDPE 50/50	447.928	20.903	918.651	21.524

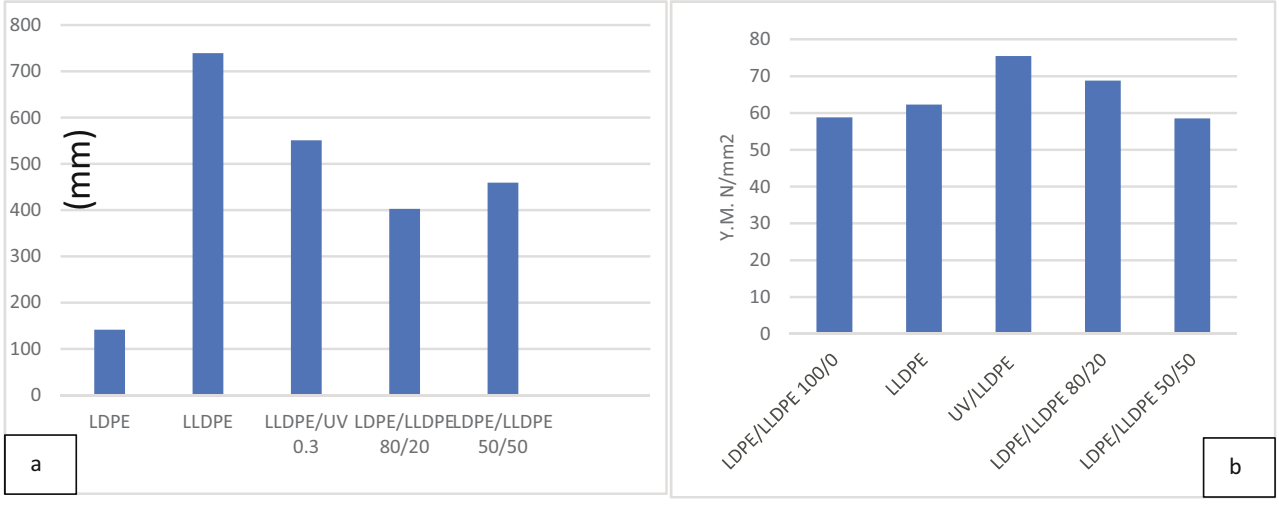

Figure 5: Comparison of the (a) elongation @ break and (b) Young's modulus for the tested samples of LLDPE.

this section, the mechanical properties of the prepared samples are investigated and compared to the changes reported in the NMR and SEM. The matrix interfaces of LLDPE and LDPE have the same monomer repeating unit, but with the side branching of LDPE that resulted in forming an immiscible mixture, which was noticed from the NMR graphs (Figures 1 and 2). A comprehensive description of the tensile and modulus values for the blend and enhanced samples with microparticle additives is provided in Table 3.

The elongation results of the breakpoint measurements and Young's modulus are presented in Figure 5. It is clear that the incorporation of microparticles has a noticeable negative effect on the elongation at the breaking point, with a decrease reaching up to 32% compared to pure LLDPE (Figure 5a). This is due to the minor restructuring of the lamella due to the adhesion of the UV stabilizer particles on the polymer matrix [27]. For the blend at low LLPDE concentrations of 20%, the elongation at the break decreases with an increasing amount of LDPE, which is expected as the LDPE dominates the structure at the interface and the short branches form more stiffness of the matrix. Furthermore, the blend interface behaves like physical crosslinking point, which restricts the movement of polymer chains and has this property in the final material [28]. As a result, they inhibit the mechanical properties of the blend, making it less flexible. It is important to mention that the interfacial forces on solid interfaces are not located on the interface itself but are distributed in their vicinity and appear as body forces.

Similarly, in Figure 5b, when the LLDPE mechanical properties are subjected to enhancement by using microfillers (UV stabilizers), Young's modulus increases over the values for LLDPE/LDPE blend samples, as shown in Figure 5b. This is because the changes in the lamella formed in the matrix due to LDPE resulted in a profoundly deleterious effect on the properties of the blend samples; such phenomena do not exist at the interface of the LLDPE with UV stabilizer microparticles. LDPE has excessive branching leading to a less tight molecular structure which causes the low density of the material. On the other hand, LLDPE has a significant number of short branches leading to less entanglement during elongation, consequently giving LLDPE higher tensile strength.

In general, weak adhesion would result in poor mechanical properties in the blends. The inferior properties of the LDPE/LLDPE blend can be confirmed from the SEM images of the blend (Figure 4a), which shows incompatibility. However, a mixed amorphous interphase is expected to present, meaning that the chains of both polymers in the blend are mixed in the amorphous phase, resulting in a stronger interphase.

4 Conclusion

Different polymer outdoor properties enhancing techniques were examined in this work in terms of structural changes and behaviour at the interface, and also the impact of these changes on the thermal and mechanical properties were examined for desert environment durability. The comparison was made between blending LLDPE with LDPE at different ratios and using microparticles (UV stabilizers) as a property-enhancing method. The NMR analysis showed a noticeable change in the blended structure compared to the microparticle additive. Using SEM, a morphology study of the selected samples revealed a reasonably weak interaction between the blend components. Moreover, the compatibility issues of the blend with higher LLDPE content were realized. Correspondingly, at low LLDPE content in the blend, the mechanical characteristics of the LDPE were dominant, whereas the TGA test for thermal property evaluation showed that the blend composition LLDPE/LDPE is thermally more stable at low LDPE content. Moreover, analysis of the mechanical properties of elongation at break and Young's modulus gave a clear picture that the microparticle additives technique can produce good properties of the matrix due to the adhesion and stability of both lamella and amorphous structures of the polymer. Wherein the blend, the immiscible characteristic of the blend, can dictate the structural changes and consequently show instability in the thermal properties and undermine some mechanical properties. The improved properties are commonly attributed to the improved adhesion at the interface of the dispersed phase and the matrix. In terms of cost and processability, the use of UV microparticles is more effective and less complex when compared with polymer blending.

Conflict of interest: Authors state no conflict of interest.

References

[1] Al-Samhan M, Al-Attar F, Al-Fadhli J, Abraham G. Thermal and rheological response to ultraviolet stabilizers additive in linear low density polyethylene under sever environmental

conditions. J Environ Sci Technol. 2019;12:213–20. doi: 10.3923/jest.2019.213.220.
[2] Noorunnisa P, AlMaadeed M. Processing and characterization of polyethylene-based composites. Adv Manuf Polym Compos Sci. 2015;1(2):63–79. doi: 10.1179/2055035915Y.0000000002.
[3] Huang X, Ke Q, Kim C, Zhong H, Wei P, Wang G, et al. Polym Eng Sci. 2007;47(7):1052–61.
[4] Basfar A, Ali K. Natural weathering for films of various formulations of low density polyethylene and linear low density polyethylene. Polym Degrad Stab J. 2006;91:437–43.
[5] Cho K, Lee BH, Hwang K, Lee H, Choe S. Rheological and mechanical properties in polyethylene blends. Polym Eng Sci. 1998;38:1969–75.
[6] Yamaguchi M, Abe S. LLDPE/LDPE blends. I. Rheological, thermal, and mechanical properties. J Appl Polym Sci. 1999;74:3153–9.
[7] Hussein IA. Melt miscibility and mechanical properties of metallocene linear low-density polyethylene blends with high-density polyethylene: influence of comonomer type. Polym Int. 2005;54:1330–6.
[8] Gupta AK, Rana SK, Deopura BL. Mechanical properties and morphology of high-density polyethylene/linear low-density polyethylene blend. J Appl Polym Sci. 1992;46:99–108.
[9] Tashiro K, Stein RS, Hsu SL. Cocrystallization and phase segregation of polyethylene blends. 1. Thermal and vibrational spectroscopic study by utilizing the deuteration technique. Macromolecules. 1992;25:1801–8.
[10] Liauw CM, Quadir A, Allen NS, Edge M, Wagner A. Effect of hindered piperidine light stabilizer molecular structure and UV-absorber addition on the oxidation of HDPE. Part 1: long-term thermal and photo-oxidation studies. J Vinyl Addit Technol. 2004;10(2):79–87.
[11] Andradey L, Hamid S. Effect of climate change and UV on materials. Photochem Photobio Sci. 2013;2:68–72.
[12] Xu J, Xu X, Chen L, Feng L, Chen W. Effect of composition distribution on miscibility and co-crystallization phenomena in the blends of low density polyethylene with conventional and metallocene-based ethylene-butene copolymers. Polymer. 2001;42:3867–74. doi: 10.1016/S0032-3861(00)00756-4.
[13] Martuscelli R, Palumbo A, Kryszwski M. Polymer blends. New York: Plenum Press; 1980.
[14] Mohammed NA. The mechanical properties and morphology of ternary blends of polyethylene. Eng Tech J. 2009;27(6):1197–202.
[15] Sui G, Fuqua MA, Ulven CA, Zhong WH. A plant fiber reinforced polymer composite prepared by a twin-screw extruder. Bioresour Technol. 2009;100:1246–51. doi: 10.1016/j.biortech.2008.03.065.
[16] Salasinska K, Ryszkowska J. The effect of filler chemical constitution and morphological properties on the mechanical properties of natural fiber composites. Compos Interface. 2015;22:39–50. doi: 10.1080/15685543.2015.984521.
[17] Flinn B, Clark B, Satterwhite J, Voast P. Influence of peel ply type on adhesion bonding of composites. In SAMPE 2008 Proceedings. Long Beach, CA; Society for the Advancement of Material and Process Engineering. 2008 June 3–7. p. 1–26.
[18] Al-Samhan M, Al-Attar F, Al-Fadhli J, Al-Shamali M. The influence of nano $CaCO_3$ on nucleation and interface of PP nanocomposite: matrix processability and impact resistance. Polymers. 2021;13:1389. doi: 10.3390/polym13091389.
[19] Hassan A, Wahit U, Chee CY. Mechanical and morphological properties of PP/NR/LLDPE ternary blend-Effect of HVA-2. Polym Test. 2003;22:281–90.
[20] American Society for Testing and Materials, ASTM test method D-638, Standard Test Method for Tensile Properties of Plastics. 2003.
[21] American Society for Testing and Materials, ASTM test method D-3850, Standard Test Method for Rapid Thermal Degradation of Solid Electrical Insulating Materials By Thermogravimetric Method (TGA); 2019.
[22] Masud M, Yu Y. Determination of the composition of LDPE/LLDPE blends via 13C NMR. Macromolecular Symposia. Vol. 390; 2020. p. 1. doi: 10.1002/masy.201900013.
[23] Ishigaki T, Sugano W, Nakanishi A, Tateda M, Ike M, Fujita M. The degradability of biodegradable plastics in aerobic and anaerobic waste landfill model reactors. Chemosphere. 2004 January;54(3):225–33.
[24] Miao Y, von Jouanne A, Yokochi A. Current technologies in depolymerization process and the road ahead. Polymers (Basel). 2021 Jan 30;13(3):449. doi: 10.3390/polym13030449. PMID: 33573290; PMCID: PMC7866858.
[25] Zhang F, Liu J, Xie F, Fu Q, He T. Polydispersity of ethylene sequence length in metallocene ethylene/α-olefin copolymers. II. Influence on crystallization and melting behavior. Polym Sci Polym Phys Ed. 2002;40:822–30.
[26] Arnal ML, Sánchez JJ, Müller AJ. Miscibility of linear and branched polyethylene by thermal fractionation: use of the successive self-nucleation and annealing (SSA) technique. Polymer. 2001;42:6877–90.
[27] La Mantia FP, Morreale M, Botta L, Mistretta MC, Ceraulo M, Scaffaro R. Degradation of polymer blends: a brief review. Polym Degrad Stab. 2017;145:79–92.
[28] Spiechowicz J, Łuczka J. Arcsine law and multistable Brownian dynamics in a tilted periodic potential. Phys Rev E. 2021;104:024132.