

Research Article

Photodegradation of UHMWPE Compounded with Annatto and Beetroot Extracts

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We observed the anti-UV action of beetroot extract in an ultra-high molecular weight (UHMWPE) matrix. The beetroot extract and the one prepared from annatto seed also acted efficiently as pigment to the same polymeric matrix. Neat UHMWPE and UHMWPE compounded with annatto and beet extract were compression molded and tensile specimens were obtained from the molded plates and submitted to UV radiation for up to 42 days. Tensile tests were performed and it was observed that the beet extract had a stabilizing action in the polymer compared to neat polymer and the one with annatto extract. Complementary analyses showed good homogenization of the extracts through the polymer matrix indicating the possibility of use as pigment, although the annatto extract appeared to be very unstable under irradiation. Spectroscopic characterization helped to explain the stability of the extracts before and after molding.

1. Introduction

The combination of synthetic polymers from oil with materials derivative from renewable sources has increased recently for many goals; between them can be cited the use of renewable source which has advantage of saving finite feedstock when substituting it, for example, when natural fiber substitutes inorganic fiber as polymeric matrix reinforcement [1–5]. Another point is an increase of the potential biodegradability of the final product by mixing a nondegradable polymer with a biodegradable component, principally by easily exposing to the environment a higher area of the nonbiodegradable component due to the pulverizing after the consumption of the biodegraded one, considering that the derivative from renewable source is biodegradable. For this case we can exemplify the blends of synthetic polymers with natural ones like starch [6–12]. It is also outstanding the cost reduction on using materials that could be discarded as in the use of straws

and husks as polymer additive [13, 14] and the replacement of toxic materials with others more environment friendly, for example, in the substitution of synthetic pigments with natural organic one and use of natural organic products as thermooxidative stabilizer [15–20]. Through these examples we can glimpse an extensive study area because of the huge combinations available due to the high variety of synthetic polymers and products from organic nature.

Annatto is a natural coloring agent obtained from the outer coats of the seeds of Brazil and other tropical countries native shrub *Bixa orellana* [21, 22]. The yellow-orange pigment produced is largely used as cosmetic, coloring agent, antioxidant of foods [21, 23–26], and so forth. The pigment is abundant of carotenoids like bixin that corresponds to about 80% of the composition of the pigment, but other components are also present like norbixin, lycopenoates, and so forth [21, 22]. The yellow-orange color provided is strictly related to molecular structure of bixin which is formed

by carbon molecules with conjugated double bonds with the presence of carboxyl groups. These structures are sites of interaction with UV radiation, what explains the short lifetime when exposed to it, resulting in discoloration [21, 27]. There are some reports of application of this pigment in textile industry involving principally natural polymers [28, 29]. On the other hand, beetroot, commonly called beet, is a root produced around the world largely, used as food and feedstock to sugar production industry [30–32], and also used as natural colorant to food industry, containing high level of biologically accessible antioxidants [33–35]. The betalains are responsible for the deep red-purple to yellow-orange color presented, being betacyanin and betaxanthin the more important two kinds [36, 37]. Sucrose is the most important kind of sugar produced by beet, but there are several other components, for example, flavonoids and acids [35, 36]. One challenge to use components like annatto and beet pigments as polymer additive is the normally high processing temperature what can degrade the components. In studies with foods and solutions, there are reports about loss of bixin and betacyanins when the temperature increases, but there is dependence of the food composition [38, 39].

Ultra-high molecular weight polyethylene (UHMWPE) is an engineering polymer with predominantly linear chains and molar mass higher than 10^6 g/mol with some grades achieving 8×10^6 g/mol. Because of the high molar mass, it is sold in powder form and has some special properties such as high impact strength and abrasion resistance [40–42]. When submitted to UV radiation, UHMWPE is photodegraded like high density polyethylene (HDPE), except for some mobility differences of radicals formed due to the molar mass difference between these two polymers, needing stabilization when used in external environment [40].

Considering the possibilities of anti-UV, prooxidant, and pigment potentials, the aim of this study was to investigate the addition of annatto and beet extract to UHMWPE and evaluate the changes on mechanical properties, color, and stability under UV radiation. Tensile specimens were submitted to UV radiation for different time intervals and the mechanical properties were monitored, beside other complementary tests.

2. Material and Methods

The UHMWPE grade used was supplied by Braskem in powder form, with molar mass of 3×10^3 Kg/mol and density of 925 Kg/m^3 . The annatto and beetroot were acquired from commerce.

0.1 L of ethanol, 0.050 Kg of annatto seed, and a magnetic bar were poured in a 0.5 L beaker. The mixture was kept under magnetic stirring and was heated at 60°C for 0.5 hours. Thereafter, the extract was obtained by filtering the mixture through a coffee filter paper, which was poured into a polypropylene pot containing 0.25 Kg of UHMWPE powder. After the polymer powder and extract homogenization, the mixture was left up to total ethanol evaporation at room temperature. During the evaporation process, the polymeric powder with the extract was periodically reversed to facilitate

the ethanol output. The whole procedure was also performed using beetroot small pieces in place of annatto. Thereby, three different compositions were obtained: neat UHMWPE, UHMWPE with annatto extract, and UHMWPE with beet extract.

Type IV tensile bars (ASTM D-638) with 2 mm of thickness were machined from plates which were molded on a Solab hydraulic press at 220°C for 40 minutes using pressure of 2.7 MPa with periodic degassing during the cycle. The cooling of the plates was done by putting them under water at room temperature.

The tensile specimens were exposed to ultraviolet radiation using LightTech 80 W fluorescent tubes which are specified to artificial sunbath, at room temperature, a similar procedure used on another study [43]. The distance from lamps to the specimens during the exposure was 70 mm; the exposure was done continually and on only one side of the specimens. For each composition, three kinds of samples were obtained according to the UV time exposure: 0, 21 and 42 days.

Tensile tests on specimens after UV irradiation were conducted in Shimadzu tensile test machine on a crosshead speed of 50 mm/min at 25°C . The data obtained were the rupture strain, the yield stress, and the elastic modulus that was considered to be the slope of stress strain curve between 5 and 10 MPa in the elastic region. At least 5 specimens were tested for each composition.

The infrared spectra were obtained in the 400 to 4000 cm^{-1} range using a Shimadzu Prestige 21 spectrometer with a horizontal attenuated reflection accessory (FTIR-ATR). The FTIR analyses were done in the polymer powder and in the surfaces of the tensile specimens after UV exposure. To quantify the changes, we determined the carbonyl index in two ranges of wavenumber: 1710 to 1740 cm^{-1} and 1731 to 1735 cm^{-1} ; hydroxyl index referent to wave number ranges between 3010 and 3780 cm^{-1} ; and the index referent to band ranges between 962 and 1200 cm^{-1} . In all these cases we determine the band area and divided the result by the reference band area, between 1330 and 1396 cm^{-1} .

UV-vis spectroscopy was performed in a Perkin Elmer Lambda 1050 spectrometer aiming at analyzing the stability of the pigments in aqueous solution (50% ethanol/50% water v/v), the wavelength range covered was 250 to 800 nm, and the scanning speed was 266.75 nm/min . The concentration of pigment to this test was much lower than what is used to prepare the tensile specimens, 353 and 708 times more diluted to beet and annatto extract, respectively. The records were done soon after the extract preparation and after 7 days of preparation. For the last one, the extracts were exposed to light (standard commercial fluorescent light) at room temperature (about 25°C), sealed with plastic film to prevent solvent evaporation.

A model SSX-550 superscan Shimadzu scanning electronic microscopy (SEM) was used to evaluate the morphology of tensile fracture surfaces of the specimens. The surfaces were sputter-coated with gold in a vacuum chamber before test. The optical microscopy of tensile fracture surfaces was done using a Instrutherm portable pen optical microscope.

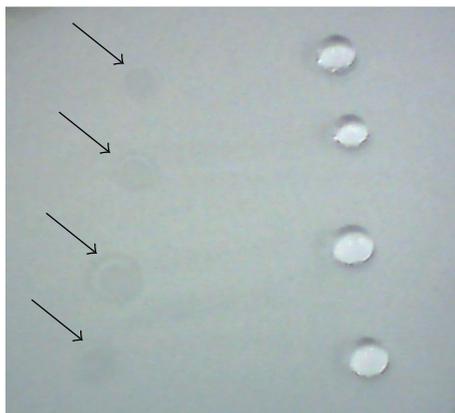


FIGURE 1: Wettability difference between ethanol and water in UHMWPE powder.

3. Results and Discussion

The visual analysis of the tensile specimens removed from molded plates indicated a homogenous distribution of the additive through the polymer, which can be assigned to the additive incorporation way. Although the ethanol is not a polyethylene solvent, it wets this polymer considerably and then promotes good distribution of the pigment through the polymeric powder after solvent evaporation, which is due to the small size of the polymer particles. In Figure 1 we see that the ethanol drops, indicated by black arrows, wet the UHMWPE powder while the water drops, on the right side, do not wet the polymer powder. Therefore, we conclude that it was an efficient way that the additive has been incorporated into the polymer. The addition of conventional stabilizers or lubricants to UHMWPE is always done through the mixing of powders because of the zero fluidity of the polymer. In the case of homogenization in molecular level, when it happens, this is done during molding. Shen et al. added natural polyphenols to UHMWPE powder and observed enhancement on the thermal stability of the product in comparison to neat UHMWPE [44]. Bridson et al. added flavonoids to linear low density polyethylene through extrusion process, but, in this case, the lower molar mass in relation to UHMWPE allowed it [20].

Figure 2 illustrates the most probable steps to good dispersion of pigment achieved through the polymer powder.

To evaluate the stability of the extracts, we obtained the UV-vis spectra which are shown in Figures 3 and 4. It can be seen that both solutions have the expected spectrum for the pigments extracts, showing the presence of bixin, peaks at 434, 457 and 480 nm (Figure 3(a)), as also found by Santos et al. and Dias et al. with annatto [25, 45], and betalain, of 477 nm peak for betaxanthin and 537 nm for betacyanin (Figure 3(b)), a result similar to that obtained by Zhang et al. with beetroot extract [46].

Figure 4 compares the stability of the extracts with the storage time. After 7 days the spectrum of the annatto extract is practically the same as that one obtained from the fresh extract, indicating the stability under the given

conditions (Figure 4(a)). Santos et al. observed changes on UV-vis spectrum of annatto extract with the way of extract preparation, for example, varying temperature and pH [25]. On the other hand, a large change after 7 days of storage to the beetroot extract in comparison to the fresh one is noted (Figure 4(b)). In fact, the changes on spectrum already occurred after 1 day of storage, although this result is not shown in Figure 4(b). The changes verified may be related to degradation processes of pigment molecules, which can be considered as being unstable in aqueous solution, with the solution changing to dark brown because of the oxidation [46]. The beetroot extract is more unstable in water [47, 48], which was not used in the preparation of extracts added to UHMWPE, although there was some of it on the extract because of the presence of water naturally in beetroot composition. The extract was added to polymer soon after being prepared without storage interval, and after molding the pigment was encapsulated by the UHMWPE, without any solvent.

From Figure 4 we can also observe that the two pigments absorb radiation in the UV region, which may be related to possible photodegradation reactions triggered by the exposure to UV radiation. The beetroot extract, over the following days, experimented an increase of the intensity of the absorption band in a more energetic radiation and a shorter wavelength. The absorption in this range may produce different effects depending on the stability of the polymer structure. It can trigger degradation processes by activating reactive groups in the case of less stable molecules, sensitizing the material, or if the structure is stable, there may be dissipation of the absorbed energy in a nonharmful way, stabilizing the material. UV absorbers with intensive absorption should be fairly stable under light exposure; otherwise it will be quickly consumed in rapid stabilizers reactions [49].

The UHMWPE with annatto extract acquired a yellow color and the specimens remained translucent like the neat UHMWPE molded plate, showing that the annatto solubilized in the polymer acted as dyestuff [50]. The molded UHMWPE with beet extract became dark brown, a different coloration from powder before molding that presented a light purple color, evidencing chemical changes on beet extract during the processing. It was possible to observe visually the presence of dispersions indicating that in this case the pigment did not solubilize totally in the polymer. However, as observed for annatto, the color presented homogeneous through the whole volume indicating success of the beet extract as UHMWPE colorant. Due to the complexity of several compounds present in the beet extract, it is difficult to explain what chemical reactions occurred during the processing that made the product dark brown. Nevertheless, we realized the tendency to acquire this color when the extract was stored during 7 days at room temperature; and here, during the processing of UHMWPE, we can assign it to the high temperature achieved, accelerating the betalains oxidation [46]. However, it is worth noting that other important reactions certainly occurred, which are also responsible for the final color of the polymer. When sugar like sucrose, present in beetroot [36], is submitted to

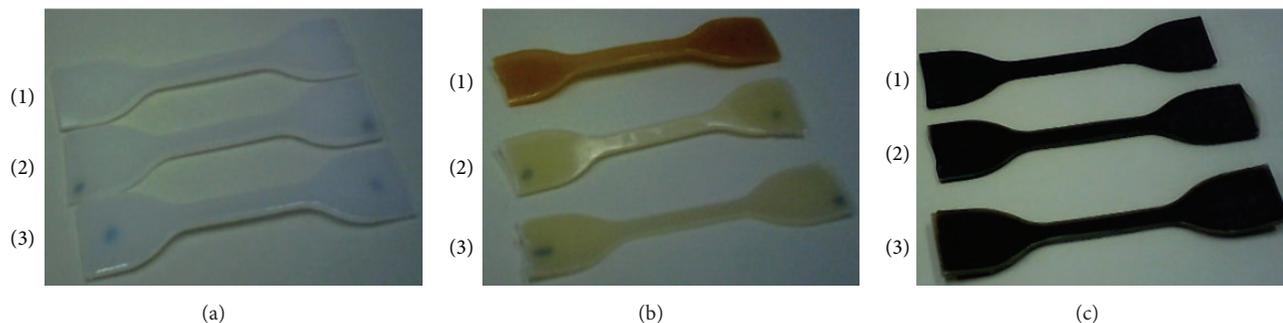


FIGURE 5: (1) Unexposed specimens, (2) exposed specimens for 21 days to UV radiation, and (3) exposed specimen for 42 days to UV radiation: (a) neat UHMWPE, (b) UHMWPE with annatto, and (c) UHMWPE with beet.

high temperatures, a process called caramelisation occurs, in which the sucrose molecules decompose resulting in dehydration and formation of several compounds, like 5-hydroxymethylfurfural [51]. The compound formed due to the caramelisation process presents a dark brown color, besides developing a characteristic odor of burnt sugar that was smelled during processing and remained in the molded polymer.

The additive solubility in the polymer matrix can be associated with chemical affinity and concentration employed. The UHMWPE is hydrophobic and the structures of components as betacyanin, betaxanthin, sucrose, and acids present in the beet extract contain hydroxyls and acids groups which make these compounds hydrophilic [36], and then the solubility in the hydrophobic matrix is limited to low concentrations added. To increase the compatibility of hydrophilic nature flavonoids with hydrophobic polyethylene, Bridson et al. used a copolymer containing polar and nonpolar parts [20]. The relative carbon long chain size of the bixin gives its hydrophobic character [38], favoring the higher solubility of the annatto in UHMWPE.

The color of the polymer containing annatto changed after 21 days of UV exposure, and it occurred apparently homogeneously through the thickness, turning the specimens light yellow and maintaining this color after 42 days; therefore for an application of long term as pigment under sunlight some mechanism of stabilization would be necessary. The polymer containing beet extract changed only a little under UV radiation, principally on the exposed surface, presenting some discoloration with the color becoming lighter. The neat polymer did not show evident changes on coloration in visual terms (Figure 5). Masek suggests the changes on coloration as an indicator of polymer ageing time [52]. Lobato et al. increased the stability of bixin to light and temperature through the nanoencapsulation in poly- ϵ -caprolactone [53]. In a study about use of natural compounds as photosensitizers to solar cells, Hug et al. point out that if protected from direct sunlight, the betalains are stable for more than a year. They also highlighted the importance of assembling the solar cell with the dye under inert atmosphere to avoid degradation of betalains [16].

Figure 6 shows the FTIR spectra from dried powders of neat polymer, blended with annatto and beet extract after

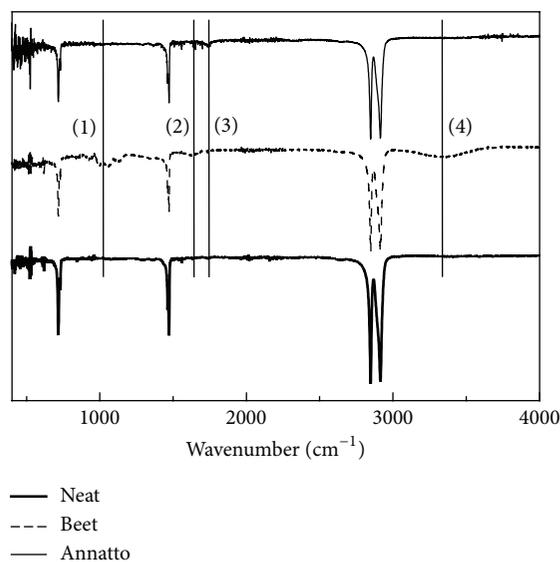


FIGURE 6: Powder's spectra from neat UHMWPE, UHMWPE with annatto, and UHMWPE with beet.

ethanol evaporation. They were plotted together to see the significant changes in relation to neat polymer after extract incorporation and they are localized through vertical lines and numbered in the plots. To the line (1), corresponding to wavenumber range between 960 and 1300 cm^{-1} , the difference was observed in the UHMWPE with beet extract spectrum and the bands can be associated to C-O bond stretching which is part of betalains, sugar, acids, and residual solvent. The new bands associated with (2) and (3) lines were observed in the two spectra with extract, are located between 1600 and 1800 cm^{-1} , and can be attributed to C=C, C=O, and C=N which are present in betalains, acids from beet and bixin from annatto. The band associated with fourth line was observed only in UHMWPE with beet extract, in 3000 to 3800 cm^{-1} range, and can be attributed to N-H and O-H stretching present on betalains, acids, sugar, and water as residual solvent from beet. Although the O-H group is also present on bixin composition, a clear band in its spectrum was not observed [22, 54].

TABLE 1: Carbonyl, hydroxyl, and the one referent to band between 962 and 1200 cm^{-1} indexes with the time exposure.

UHMWPE	Carbonyl index 1710–1740 cm^{-1}	Carbonyl index 1731–1735 cm^{-1}	Hydroxyl index 3010–3780 cm^{-1}	Band index 962–1200 cm^{-1}
		Powder		
Neat powder	0.227	0.049	7.350	—
Annatto powder	0.200	—	—	0.178
Beet powder	0.539	0.181	472.9	87.89
		Specimens		
Neat 0 day	0.332	0.025	—	1.740
Neat 42 days	0.344	0.076	12.07	4.488
Annatto 0 day	0.101	0.013	4.102	3.803
Annatto 21 days	0.197	0.019	7.759	9.385
Annatto 42 days	0.591	0.073	6.097	8.499
Beet 0 days	0.541	0.093	12.70	2.863
Beet 42 days	0.269	0.009	4.849	4.214

To measure some chemical changes occurring during processing and in the UV exposure through FTIR, we calculated the carbonyl index in two wavenumber ranges, hydroxyl index and the index related to band located between 962 and 1200 cm^{-1} . The most important remarks from Table 1 are the carbonyl and hydroxyl indexes increasing with the time exposure to neat UHMWPE and to composition with annatto, indicating that the oxidation level increased. Nonetheless to polymer with beet the carbonyl and hydroxyl indexes decreased with the time exposure showing that the extract decomposition with carbonyl and hydroxyl groups removal overcame the polymer oxidation. The initial high level of carbonyl and hydroxyl groups on composition with beet extract is confirmed by the large value of the carbonyl and hydroxyl indexes for the powder of this formulation. The increase of the hydroxyl index in polyolefins indicates oxidation due to the increase of the hydroperoxides and hydroxyls terminals, but the reduction observed in composition with beet can be attributed to dehydration, water evaporation, between other hydroxyls elimination ways during the processing. It is well known that the oxidation of polyolefins occurs predominantly at surface because of the oxygen accessibility [55–57]. In relation to band between 962 and 1200 cm^{-1} and considering that it represents the evolution of C-O groups, the tendency, in general way, is the same as observed to the other two indexes.

The oxidation process of UHMWPE begins with a free radical formation on one chain, in this study due to the UV radiation incidence. The propagation occurs by peroxidic radical formation through free radical and oxygen reaction, reaction of peroxidic radical with a second chain with hydrogen withdraw, forming a free radical on the second chain and hydroperoxide on the first one. The following step is the decomposition of hydroperoxide having as consequences, in general way, chain scission with definitive groups containing oxygen in chain structures, commonly carbonyl and hydroxyls. When irradiated without presence of oxygen, the UHMWPE crosslinks predominantly [40, 58].

The stress strain curves of neat and compounded with beet and annatto extract UHMWPE after different UV exposure time are shown in Figure 7, where we can see that the behavior depends on the composition. The stress strain curves (Figure 7(a)) of the neat polymer showed many differences with the increase of UV time exposure. The unexposed neat polymer curve is a typical UHMWPE curve in which although the total strain is high, there is no stress reduction on the yielding point meaning the absence of necking and the plastic region presenting a continuous rise on stress with no cold drawing region that is typical on polyethylenes with lower molar mass [59]. After the 21 days of UV exposure, the polymer still presents high ductility but the curve shows an increase on stress at the yielding point and the showing-up of a cold drawing region attributed to the crystallinity raise and the entanglement density reduction, which are two effects of photodegradation [59, 60]. After 42-day exposure, the polymer presented only elastic strain and the stress value on rupture indicates that the crystallinity increased in relation to polymer irradiated for 21 days. In summary, the UV radiation promoted the polyethylene degradation with changes on mechanical properties caused by surficial oxidation, molar mass reduction, and increase in the degree of crystallinity [61, 62]. To the polymer compounded with beet extract (Figure 7(b)), except the minor rise on stress at the yielding point with the UV exposure time, the curves almost overlapped for all exposure times, indicating that the beet extract acted efficiently as UV stabilizer. We can also see through the unexposed sample that the addition of beet extract to the polymer did not change the stress strain behavior in relation to neat UHMWPE, a behavior similar to the observed one when using conventional stabilizers, because of the low content. Regarding formulation with annatto (Figure 7(c)), we can see that the polymer was susceptible to degradation, showing fragile behavior after 42 days of UV exposure, and even the unexposed sample presented inferior properties as elongation and tensile strength at the break in comparison to neat polymer.

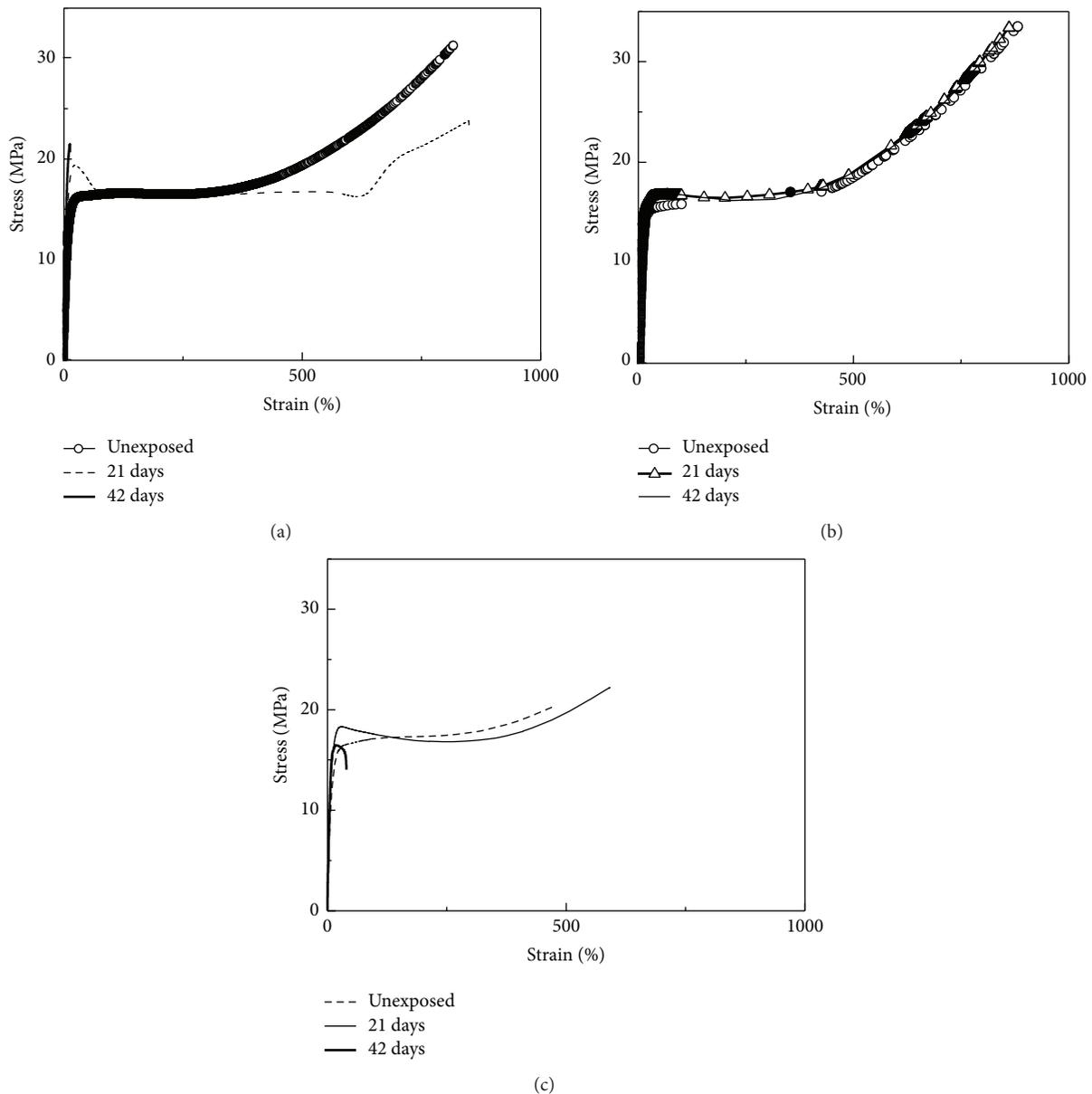


FIGURE 7: Stress strain curves in different times of UV exposure from (a) neat UHMWPE, (b) UHMWPE with beet extract, and (c) UHMWPE with annatto extract.

The curves of different compositions were plotted together for the same time of UV exposure and then we could compare the influence of the composition (Figure 8). To the unexposed samples, it is clearly shown that the annatto addition to UHMWPE reduced the strain at the break but the ductility is still high, and the neat polymer has similar behavior to the composition with beet (Figure 8(a)). The annatto addition interfered on the plastic strain so that the rupture strain reduced from 800 to 600%. The cause of that may be the contamination presence due to inefficient filtration of the extract, acting as stress raiser or considering the bixin molecular structure and the solubility observed in UHMWPE, the presence of this small molecules with rigid structure caused the ductility reduction because of the ends chain increase and interference on slipping between

polyethylene molecules; but we have to investigate these proposals in future studies.

After 21 days the neat polymer and the composition with annatto were more susceptible to radiation (Figure 8(b)), which intensified after 42 days of UV exposure (Figure 8(c)). However, the composition with beet remained unchanged, showing that the beet extract acted effectively as an anti-UV stabilizer. Bridson et al. observed that tannin acted as a UV stabilizer to linear low density polyethylene [20]. Shibata and Tomita observed the increase on oxidation strength due to the γ -irradiation of UHMWPE after adding α -tocopherol to the composition [63].

The molecules used as conventional UV stabilizers to polymers have aromatic structure [64]; then, comparing to betalains, sucrose, and bixin we conclude that beet extract

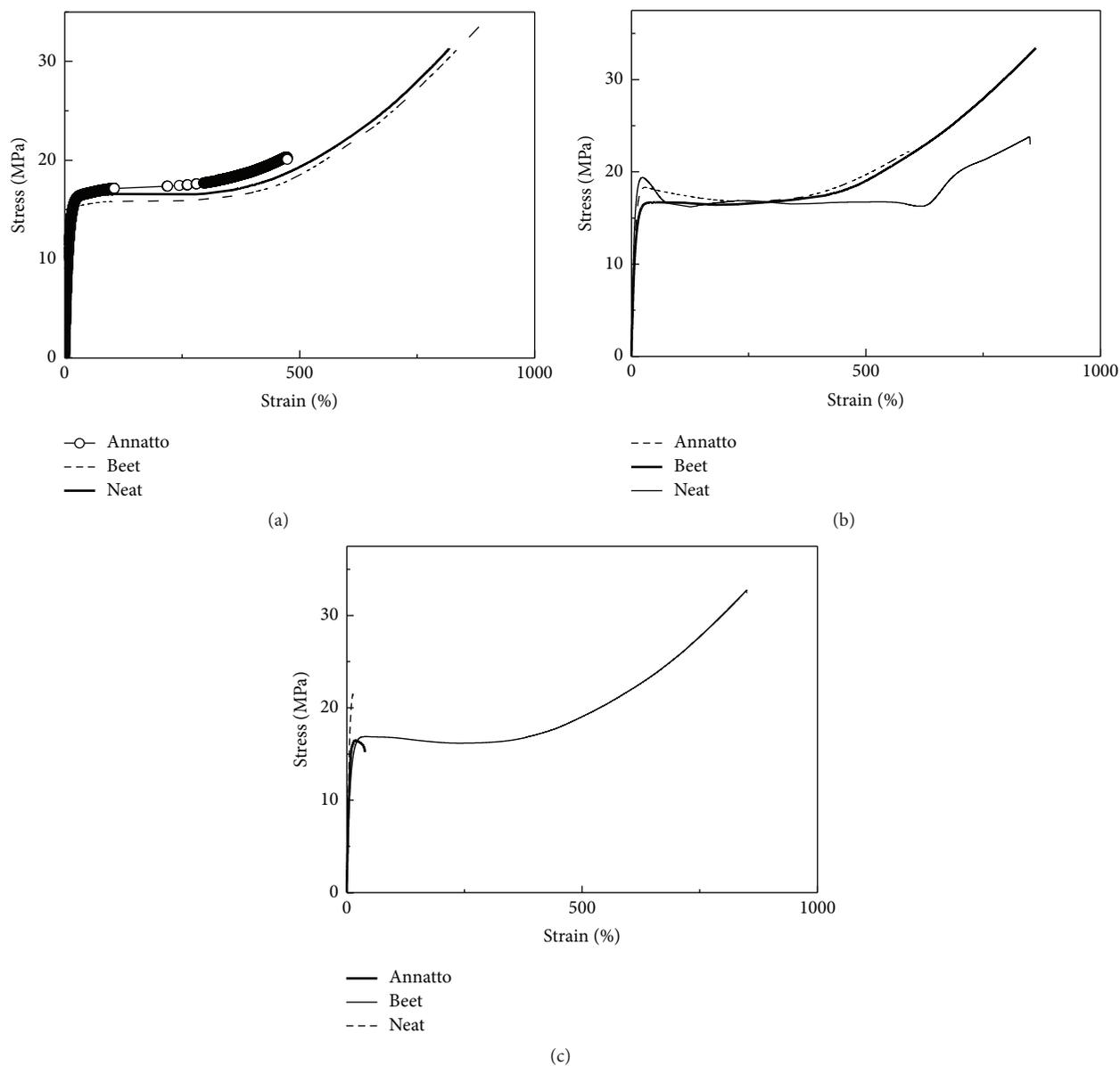


FIGURE 8: Stress strain curves for different compositions. (a) Unexposed, (b) 21 days of UV exposure, and (c) 42 days of UV exposure.

has compounds in its structure that are more alike to conventional stabilizers. In many studies about foods we saw the citation of annatto as antioxidant [26, 28]. There is no doubt about the UV absorption power of bixin, but due to the aliphatic nature we can suppose that it tends to decompose easily and can contribute to radical formation and oxidation. The complex composition of beet extract resulted in more efficient UV absorption, resulting in partial decomposition of the compounds, demonstrated by the carbonyl index reduction, what protected the polymer more efficiently. The sucrose caramelisation process that occurred during the UHMWPE with beet extract molding apparently favored the stabilization mechanism. Benjakul et al., in a study with fish mince, observed that the UV absorption increased for

4 different kinds of sugar when they were caramelised. This process resulted in scavenging radical's efficiency [65].

Some important data from tensile tests are summarized in Table 2. The rupture strain reduced when the annatto was added to UHMWPE, and under UV radiation the composition with beet did not show any change, unlike the neat and UHMWPE with annatto in which after 42 days of UV exposure the rupture strain reduced dramatically. Polyolefins like polyethylenes and polypropylenes degrade under the UV or other kinds of radiation like gamma; for example, one of the consequences is the increase of crystallinity degree due to the crystallization of broken segments on amorphous region [62, 66]. On the other hand, there is a direct relation between crystallinity degree and properties like elastic modulus and

TABLE 2: Properties obtained in tensile tests.

Sample code	Rupture strain (%)	Yield strength (MPa)	Elastic modulus (MPa)
Neat UHMWPE			
Unexposed	806 ± 37.1	16.3 ± 0.2	128.4 ± 5.8
21 days UV exposed	839 ± 80.1	19.6 ± 0.3	239.3 ± 14.1
42 days UV exposed	14.6 ± 1.7	20.2 ± 1.0 ^a	321.3 ± 14.1
UHMWPE with annatto			
Unexposed	589.0 ± 153.4	15.9 ± 0.4	109.3 ± 9.0
21 days UV exposed	578.0 ± 44.8	17.8 ± 0.6	174.0 ± 11.5
42 days UV exposed	43.7 ± 7.8	17.1 ± 0.6 ^{**}	226.8 ± 9.1
UHMWPE with beet			
Unexposed	852.5 ± 48.6	15.7 ± 0.3	110.0 ± 4.8
21 days UV exposed	848.7 ± 78.5	16.4 ± 0.2	130.4 ± 5.7
42 days UV exposed	843.2 ± 47.1	17.1 ± 0.2	154.6 ± 9.6

^aIn fact the specimens ruptured before yielding. ^{**}Localized yielding due to multiple cracks.

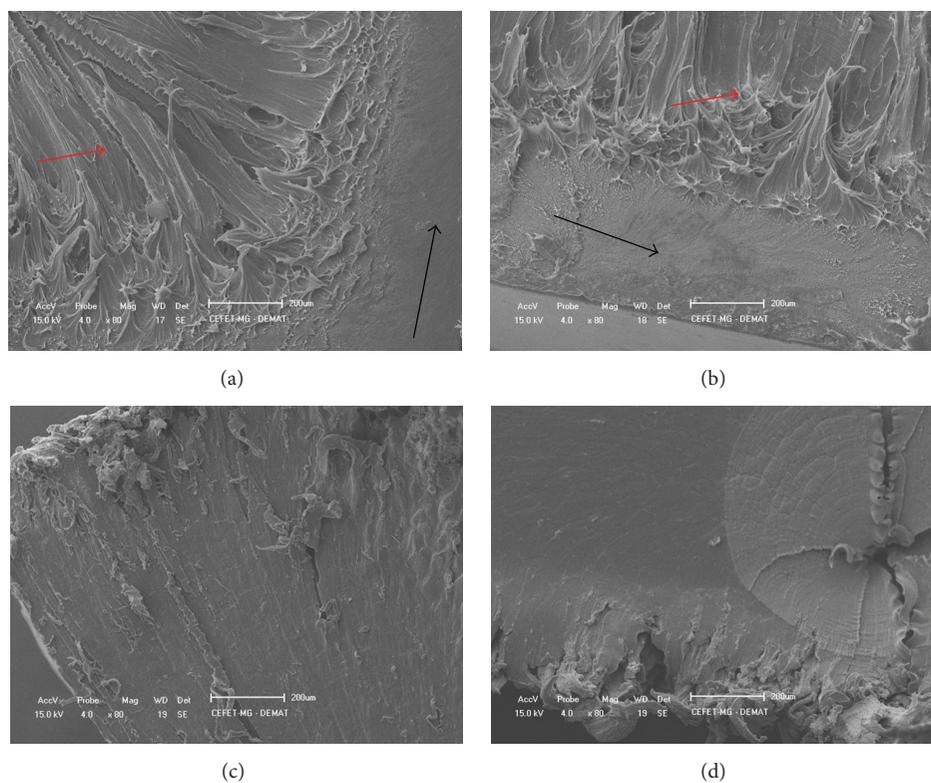


FIGURE 9: Fracture surface of tensile specimens after stress strain test: (a) UHMWPE with annatto after 42 days of UV exposure, (b) neat UHMWPE after 42 days of UV exposure, (c) UHMWPE with beet after the same time of UV exposure, and (d) UHMWPE with annatto after 21 days of UV exposure.

yield strength [45, 67]. Through the data shown in Table 2 we see that the yield strength and elastic modulus increase with the UV exposure time for all compositions, but the increase was lower to the UHMWPE with beet. For example, the elastic modulus increased more than 150% to neat UHMWPE, more than 100% to UHMWPE with annatto, and only 40% to UHMWPE with beet. The increase of these two properties favors the polymer embrittlement.

The fracture surface of tensile specimens after stress strain test is shown in Figure 9. Figure 9(a) referred to UHMWPE with annatto after 42 days of UV exposure where we can see the presence of two regions, one with high plasticity indicated by the red arrow, localized in central part of the specimen, and the other characterized by smoothness indicated by the black arrow, localized next to the surface of the sample. The latter is a degraded layer, typical from photooxidation

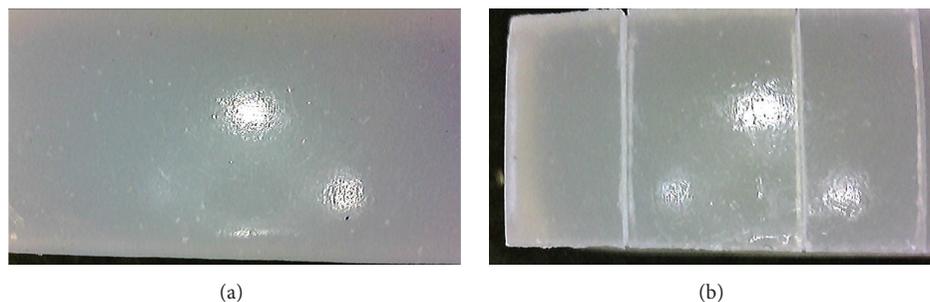


FIGURE 10: 42-day irradiated specimens after tensile tests. (a) Neat UHMWPE; (b) UHMWPE with annatto.

that occurs heterogeneously, being more intense on surface because of the oxygen accessibility [68]. This layer acts as stress riser, turning the polymer to be fragile because it is the place where the fracture originates and propagates to the internal region that was not degraded then presenting high plasticity, but only on local level, as the total rupture strain was small. The fracture surface of neat UHMWPE after 42 days of UV exposure shows a similar aspect to the one shown by that compounded with annatto, but the smooth region has a higher thickness, as confirmed after inspection of the other specimens (Figure 9(b)). A completely different aspect is observed on fracture surface of the UHMWPE with beet after the same time of UV exposure (Figure 9(c)) and UHMWPE with annatto after 21-day exposure (Figure 9(d)); the aspects observed are typically from surfaces formed after high plastic strain during the tensile test, with fibrous aspect and stretched regions and typically from polymers fractured after high plastic strain, without the presence of two different regions [69].

Although we can point some similarity between the neat UHMWPE and UHMWPE with annatto as to degradation behavior, some differences exist between them, as the lower increase on elastic modulus and yield strength, the higher rupture strain after 42 days of UV exposure and the lower thickness of degraded layer to the UHMWPE with annatto in relation to neat UHMWPE. Another difference registered between the UHMWPE with annatto and neat UHMWPE, both submitted to UV radiation for 42 days, was the final appearance of the specimens after the tensile test, as shown in Figure 10. The specimens of UHMWPE with annatto presented multiples cracks after test (Figure 10(b)) while the specimen of neat UHMWPE (Figure 10(a)) did not show cracks. This difference justifies the higher rupture strain of UHMWPE with annatto; the energy was dissipated in many local sites resulting on a higher total strain. Figure 10 shows patterns of horizontal cracks after photooxidation as observed in other studies [61, 68].

4. Conclusion

The annatto and beet extracts acted well as pigment of UHMWPE, with good distribution through the polymer. The beet extract acted well as anti-UV stabilizer and even after 42 days of UV exposure the polymer preserved the mechanical properties, while the neat UHMWPE and UHMWPE with

annatto extract degraded considerably. The annatto extract presented low stability under UV radiation with the compound discoloring after 42 days of UV exposure.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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