CELLULOSE CHEMISTRY AND TECHNOLOGY

INFLUENCE OF DIFFERENT FILLERS ON THE BEHAVIOUR OF LDPE-BASED COMPOSITES TO ACCELERATED WEATHERING

IULIANA SPIRIDON and RALUCA NICOLETA DARIE-NITA

"Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy,
41 A, Grigore Ghica Voda Alley, 700487 Iasi, Romania
✉ *Corresponding authors: R. N. Darie-Nita, darier@icmpp.ro; Iuliana Spiridon, spiridon@icmpp.ro*

To the memory of Acad. Cristofor I. Simionescu,
for the significant impact of his work in the field of cellulose chemistry
in Romania and beyond

Some polyethylene/wood and polyethylene/lignin formulations were prepared *via* melt blending and characterized. Their mechanical properties, thermal behaviour and surface modifications were evaluated before and after accelerated weathering. Also, the effect of incorporated fillers on the morphological properties was assessed by optical microscopy. An improved compatibility with the polyethylene matrix was recorded for the composite containing lignin and maleated polyethylene due to partial esterification of lignin. The obtained results revealed a slight effect of photostabilization of lignin during accelerated weathering.

Keywords: composites, eucalyptus wood, lignin, accelerated weathering

INTRODUCTION

The researchers' increased interest in obtaining new materials with improved properties is highly influenced by economic and environmental reasons. Thus, the design of materials based on biopolymers offers both the preservation of fossil-based resources and a solution to some environmental problems. Lignocellulosic materials have a major potential to replace plastics and materials based on fossil resources. That is why, the use of wood or its components as a filler for a plastic matrix presents high interest.[1-4]

Polyethylene (PE) is the most widely used polyolefin, due to its physico-chemical and mechanical properties. Its high availability, low cost, good mechanical and thermal properties recommend PE for various applications. Eucalyptus is a fast-growing softwood tree that could replace hardwood species in different applications.

Lignin is a renewable polymer separated from a variety of biomass sources by different delignification processes, and is used under the tag of "waste material". Its availability and aromatic structure, as well as the variety of its potential modifications, make this polymer very attractive for numerous applications. It was used as filler for commodity thermoplastics[5] or bioplastic matrices.[6-7] Its reactivity and functional groups influence the final properties of the end product. Due to its grafting and crosslinking abilities, lignin has found applications in polyurethanes, adhesives, asphalts or phenol–formaldehyde resin formulations.[8]

Fillers are often used for compounding with polymeric materials in order to improve their mechanical or thermal performances. Exposure to UV radiation can cause changes of the surface of the composites by photodegradation. The combination of UV radiation, moisture and temperature can damage both the lignocellulosic network and the polymer matrix, thus limiting the performance of the composites and their applications.

The aim of our study was to determine the influence of two fillers (lignin and eucalyptus wood) on some properties of LDPE-based composites.

Melt processing parameters, surface modifications, mechanical and thermal properties

Cellulose Chem. Technol., ***51*** *(9-10), 831-838(2017)*

were assessed to evaluate the behaviour of the composite materials to accelerated weathering.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) of A22FMA/002 type (obtained from Petrom S.A., Romania), with density between 0.91-0.93 g/cm^3, a melt flow index of 0.3 g/10 min and a degree of crystallinity of 40-50%, was used as matrix, while maleic anhydride grafted polypropylene (MAPE), Licomont AR 504 (Clariant GmbH, Germany), was used as coupling agent.

Eucalyptus wood fibres of about 0.42 mm length (washed with distilled water for 1 h under constant stirring at 80 °C and dried in an oven at 100 °C until constant weight was reached), as well as LignoBoost lignin, obtained after acid precipitation (with CO_2) of black liquor from the kraft delignification of softwood, were used as fillers.

Blending

Before compounding, the eucalyptus wood fibres and lignin powder were pre-dried at 80 °C in a vacuum oven until constant weight was reached. Compounding was performed at 145 °C for 10 min, at a rotation speed of 60 rpm, using a fully automated laboratory Brabender station.

For mechanical characterization, specimens were prepared by compression moulding using a Carver press at 145 °C (with a pre-pressing step of 3 min at 50 atm and a pressing step of 2 min at 150 atm).

The obtained formulations were denoted as follows: LDPE (as reference sample), LDPE/10EW, comprising LDPE and 10% of eucalyptus wood fibres (EW); LDPE/10EW/3MAPE, comprising LDPE, 10% of eucalyptus wood fibres (EW) and 3% maleic anhydride grafted polyethylene (MA-g-PE) as compatibilizer; LDPE/10LB, comprising LDPE and 10% of Lignoboost lignin; LDPE/10LB/3MAPE, comprising LDPE, 10% of Lignoboost lignin and 3% maleic anhydride grafted polyethylene (MA-g-PE) as compatibilizer.

Processing behaviour was evaluated from the torque-time curves recorded during the processing on the Brabender mixer.

Weathering

The weathering process was performed in a climatic chamber (CH 250 Angellantoni Ind., Italy) with artificial light from a mercury lamp ($200 < \Lambda < 700$ nm, incident light intensity of 39 mW/cm^2) at a temperature of 40 °C and 65% humidity. The exposure time was 600 hours.

Optical microscopy

The morphological aspect of the composites in melt state was observed by means of a Leica DM4500P optical microscope (Wetzlar, Germany), provided with a Linkam LTS 350 heating plate. All the systems were heated up to 145 °C with a heating rate of 10 °C/min, then the composites were kept for 2 minutes, while the photographs were recorded. A magnification of 10X was used for observation.

Surface modifications after accelerated weathering were evaluated from images recorded by means of a Leica DM2500M microscope (Germany), with a magnitude of 50X.

Mechanical properties

Before testing, the specimens were conditioned for 24 h at 50% relative humidity and 23 °C. The tensile strength, elongation at break and Young's modulus were determined according to EN ISO 527:2012. An Instron 5 kN test machine operated at a crosshead speed of 10 mm/min was used for testing the specimens. The Charpy impact strength of the composites was measured according to EN ISO 179:2001. A CEAST testing machine with a pendulum of 50 J was used to measure the unnotched specimens. The results for both mechanical tests represent an average of ten measurements.

Thermal properties

Thermal behaviour was evaluated by DSC measurements. They were performed under nitrogen atmosphere by using a TA instrument from Perkin-Elmer (USA), Pyris Diamond model, which is a power-compensated type. The DSC apparatus was calibrated with Indium before the experiments. The samples were enclosed in Al crimped pans, and dry N_2 gas was purged through the cells at a flow rate of 20 mL/min, at a heating rate of 10 °C/min. The heating scans were performed on about 7 mg of sample in the temperature range of 25-800 °C. The degree of crystallinity of the LDPE samples was obtained by dividing the melting enthalpy of the sample by 287.3 J/g,[9] which is the estimated melting enthalpy of a polyethylene with 100% crystallinity. The crystallinity of the composite materials was estimated as a function of the LDPE fraction in the composite and the melting enthalpy.

RESULTS AND DISCUSSION

Processing behaviour

The processing behaviour of the obtained blends was assessed from the torque values at different mixing time and at the end of mixing (Table 1). The viscoelasticity is controlled mainly by the polyethylene matrix and the adhesion between the additives and the matrix.

The friction of the rotors with the unmolten polymer at the beginning of processing caused high values of initial torque for all the systems (TQ_{max}). As the wood filler and lignin became very well dispersed in the LDPE matrix, the torques started to decrease significantly and remained almost unchanged at a particular level until the end of the total mixing time.

The incorporation of eucalyptus wood particles and lignin into blends affected the melt processing characteristics in a similar way, generally leading to a decrease. Moreover, the same value was recorded at the end of the mixing time for both fillers. The presence of lignin improved the melting behaviour, while the presence of MAPE led to a slight increase of melt viscosity for the LDPE/10EW/3MAPE blend, due to the chemical reactions between the functional groups of MAPE and wood.

Partial esterification of LB took place when reacting with MAPE, the composite LDPE/10LB/3MAPE displayed lower torque values in the mixer and overall better melt flow characteristics, compared to the other blends and to neat polyethylene. Also, this blend exhibited augmented compatibility and less phase separation with polyethylene.[10]

Overall, one can mention that the incorporation of eucalyptus wood fibres and LB powder in a polyethylene matrix, together with MAPE, did not change the processability of the matrix, so that the processing method was not modified for obtaining these composites.

Table 1
Processing characteristics of studied blends

Sample	TQ_{max} (Nm)	$TQ_{1\ min}$ (Nm)	$TQ_{5\ min}$ (Nm)	TQ_{fin} (Nm)
LDPE	47.3	27.6	23.7	21.3
LDPE/10EW	41.0	23.6	21.5	20.7
LDPE/10EW/3MAPE	37.6	23.8	22.4	21.6
LDPE/10LB	38.6	23.2	21.6	20.7
LDPE/10LB/3MAPE	36.5	22.8	20.9	19.3

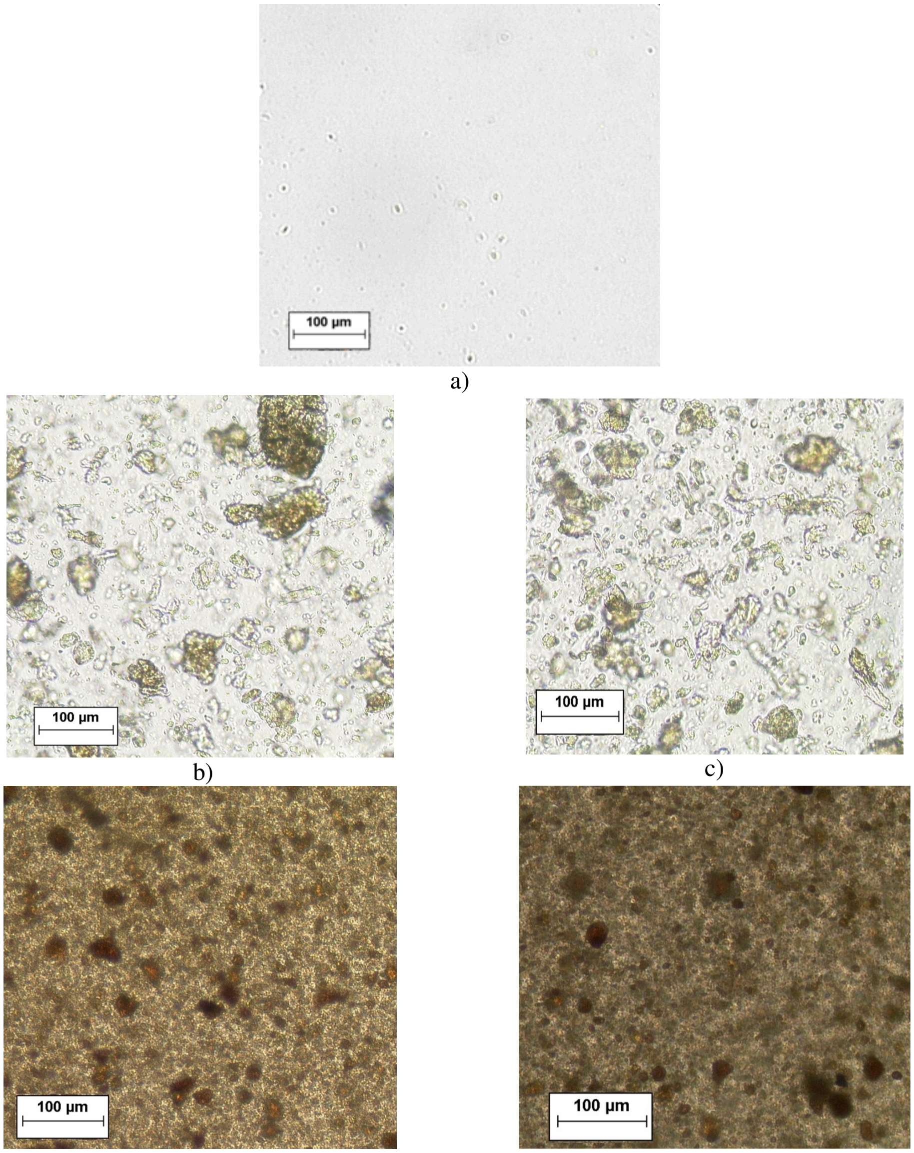
TQ_{max} = maximum torque; TQ_{1min} = torque after 1 min of processing; TQ_{5min} = torque after 5 min of processing; TQ_{final} = torque at the end of processing

Optical microscopy

Mechanical properties are directly correlated with a material's internal structure, therefore optical microscopy in melt state is a useful technique for evaluating the dispersion of particles and adhesion within the matrix.

Figure 1 shows micrographs of the studied composites comprising wood and lignin, recorded at 145 °C, in the melt state of the LDPE matrix. One can observe the transparency of LDPE in Figure 1a, and the dispersion of the wood inside the polymeric matrix in Figure 1b and 1c. In the case of the LDPE/10EW system, larger particles or even a few aggregates can be found with dimensions in the range of 10-90 µm, but with a uniform distribution. The presence of compatibilizer led to the decrease of the wood particle sizes and to the disappearance of larger aggregates or their decrease to maximum 68 µm. The enhancement of properties for the LDPE/10EW/3MAPE composite is related to an improved distribution of the wood particles within LDPE.

A similar behaviour could be noted for the composites containing lignin (Fig. 1c and d). The role of MAPE was detected in the reduction of lignin particle sizes from 10-30 µm in LDPE/10LB to about 3-20 µm in LDPE/10LB/3MAPE. A special observation in the latter system consisted in the general diminution of lignin particles and their homogeneous spreading in the LDPE matrix, although one or two aggregates could be observed. The lignin tends to form hydrogen-bond type intermolecular linkages due to its polarity, but in the presence of maleated polyethylene, the chemical structure of lignin is modified due to the partial esterification of OH groups, improving the compatibility with non-polar polyolefins.[11]



a)

b) c)

d) e)

Figure 1: Optical micrographs of a) LDPE, b) LDPE/10EW, c) LDPE/10EW/3MAPE, d) LDPE/10LB, e) LDPE/10LB/3MAPE

Mechanical properties

The increase of Young modulus for the formulation comprising wood fibres can be related to the polymer–wood components interactions. It is in agreement with the results for elongation at break. Non-exposed LDPE presented the largest elongation at break, due to its high amorphous fractions, as well as to its longer chains, which enable chain flexibility. In comparison with the LDPE matrix, a drastic loss in elongation at break was registered for the formulation comprising wood fibres, due to the restriction of the relative movement of the polymer molecules. An opposite effect was recorded for the composite comprising Lignoboost lignin (Table 2). An improvement in tensile strength by about 33% upon the addition of lignin particles indicates the reinforcing effect of lignin in the LDPE matrix, and may be explained by the adhesive nature of lignin and its crosslinking ability. As compared to the matrix, the tensile strength increased by 6% and Young's modulus by about 15%. The influence of MAPE in the concentration used was not significant.

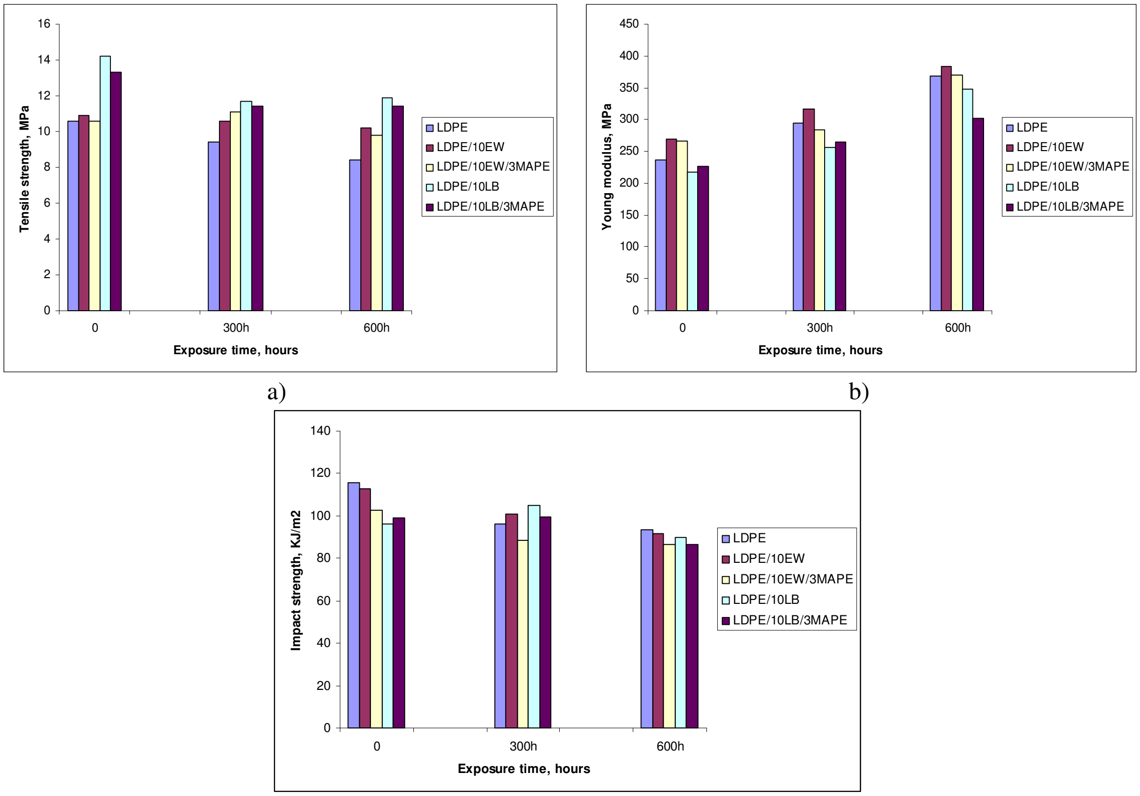
The impact strength reflects the ability of a material to resist impact, namely its toughness. As compared with the LDPE matrix, all the materials recorded a decrement in this parameter. The presence of MAPE improved the impact strength of the formulation with EW by about 17% and that of the formulation with LB by 3%. Maleic anhydride groups in the MAPE act as coupling agents and covalent bonds could be created between the filler particles and the LDPE matrix. The chemical bonding between the anhydride and the hydroxyl groups caused a better stress transfer from the matrix to the wood, leading to higher impact strength.

After weathering, all the mechanical properties (Fig. 2) affected as a function of the composite formulations.

It is well known that lignin can act as a free radical scavenger and can prevent the oxidation reaction due to its aromatic structure and multifunctional side groups.[12] This effect is evidenced in the case of the samples comprising lignin after exposure to accelerated weathering.

Table 2
Mechanical properties of composite materials as a function of composite formulation

Sample	Impact strength (kJ/m^2)	Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (mm)
LDPE	115.2±1.3	254.1±2.7	10.6±0.9	142.0±0.9
LDPE/10EW	84.3±0.9	269.2±3.2	10.8±1.3	93.5±1.3
LDPE/10EW/3MAPE	102.6±2.4	266.5±1.2	10.6±2.1	97.0±3.2
LDPE/10LB	96.1±0.9	216.5±2.9	14.2±1.7	149.0±1.7
LDPE/10LB/3MAPE	98.8±1.5	226.4±1.7	14.3±2.3	158.0±2.4



a)

b)

c)

Figure 2: Mechanical properties of composite materials before and after accelerated weathering, a) tensile strength; b) Young's modulus; c) impact strength

As may be noted in Figure 2, the tensile strength decreased for all the materials after exposure to the combined action of humidity, temperature and UV light. As compared to the unexposed samples, the decrement was of 20.7% for LDPE, 6.4% for LDPE/10EW, 7.5% for LDPE/10EW/3MAPE, 16.2% for LDPE/10LB and 14.2% for LDPE/10LB/3MAPE. It seems that the presence of MAPE had a positive influence, especially for the formulation comprising lignin.

Although the impact strength of all the materials decreased after weathering, it did not become higher than that of the LDPE matrix, the highest drop being recorded for LDPE (19.2%) and the lowest for LDPE/10LB (6.5%). The composites containing MAPE presented the lower impact strength because of the double bond breakage as a result of exposure to the combined action of temperature, UV radiation and humidity.

The incorporation of lignin into the composites also strongly influenced their thermal behaviour.

The thermal behaviour of the composite materials is of paramount importance and the incorporation of different fillers into the matrix polymers resulted in a modification of their thermal stability. Thus, the thermal stability of the materials was improved when lignin was added into the LDPE matrix. Due to its antioxidant ability, lignin can delay the degradation of polymers at elevated temperatures.[13] When lignin was added to the LDPE matrix, Tm increased by about 8.5 °C, while wood addition resulted in an increase of only 1.5 °C.

Also, DSC data showed a slight increase in crystallinity values upon the addition of fillers into the polymer matrix. The presence of wood particles increased the crystallinity of the materials by 3.2%. It was assumed that the wood particles acted effectively as a nucleating agent.

It was found that, in the formulations containing lignin, the crystallinity of LDPE decreased more, as compared to the formulations comprising eucalyptus, due to the amorphous character of lignin. After exposure to accelerated weathering, an increase of LDPE crystallinity in all the formulations was recorded. The highest increment was registered for LDPE (62.39%) and the lowest (23.69%) for the LDPE/10EW/3MAPE system (Table 3). The degradation of LDPE upon weathering results in some radical-based photochemical reactions, including molecular chain scission, as well as the release of short chains from the amorphous regions. These short chains have enough mobility to rearrange into a crystalline phase, which led to an improvement of crystallinity. Also, the shortening of the LDPE chains resulted in the decrease of the melting temperature for all the formulations, as compared with that of the unexposed formulations.

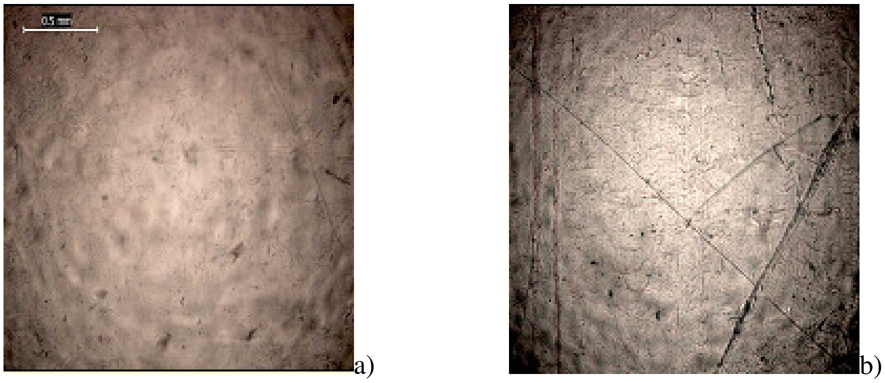
It is well known that exposure to UV results in the dissociation of C-C and C-H bonds and breaks the polymer chains, causing deterioration. Photo-oxidation ageing, which is governed by the diffusion of O_2 in the thickness of the sample, determines the occurrence of surface cracks, which can propagate into the specimen and increase the degradation of the surface exposed to UV radiation.[14-15]

This fact is evidenced by some optical micrographs of the exposed materials presented in Figure 3.

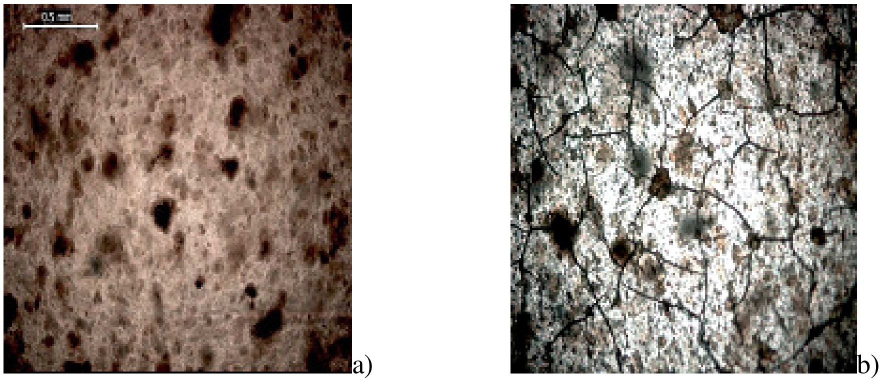
Table 3
DSC parameters of the studied materials

Sample	Tm (°C)	Xc (%)	Tm (°C) after exposure to accelerated weathering	Xc (%) after exposure to accelerated weathering
LDPE	107.7	34.3	104.9	55.7
LDPE/10EW	109.2	37.5	105.1	49.9
LDPE/10EW/3MAPE	111.2	39.0	104.8	48.2
LDPE/10LB	116.2	32.9	109.9	44.8
LDPE/10LB/3MAPE	117.7	33.6	107.4	43.9

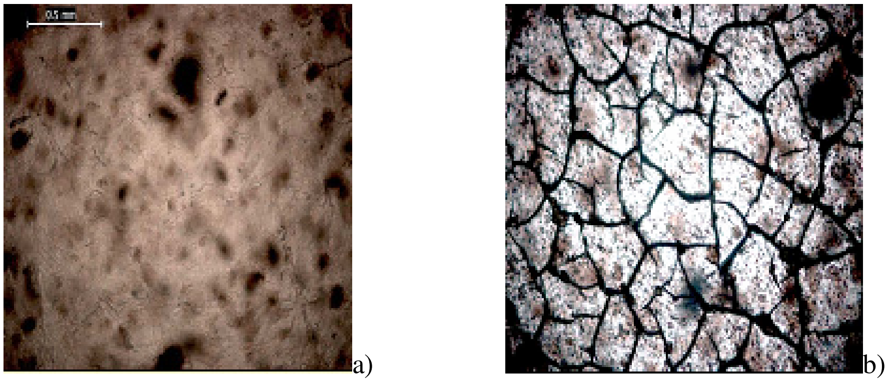
Tm – melting temperature; Xc – crystallinity index



LDPE



LDPE/10EW



LDPE/10EW/3MAPE

Figure 3: Optical micrographs of some studied materials before (a) and after (b) accelerated weathering

CONCLUSION

In spite of the fact that lignin is still considered a low-value residue its structure and availability make it suitable for numerous valuable applications.

Our results evidenced that lignin tends to form hydrogen-bond type intermolecular linkages due to its polarity, but in the presence of maleated polyethylene, the chemical structure of lignin is modified due to the partial esterification of OH groups, improving the compatibility with non-polar polyolefins. On the other hand, the presence of compatibilizer led to the decrease of wood particle sizes and to the disappearance of larger aggregates or their decrease to maximum 68 µm.

The incorporation of 10% of lignin into the LDPE matrix slightly increased its thermal stability. DSC data showed a slight increase in crystallinity values upon the addition of fillers into the polymer matrix. The exposure to accelerated weathering resulted in the increase of LDPE crystallinity in all formulations.

Although the impact strength of all the materials decreased after weathering, it did not become higher than that of the LDPE matrix, the lowest drops being recorded for LDPE/10LB (6.5%). The composites containing MAPE presented lower impact strength because of the double bond breakage as a result of the exposure to the combined action of temperature, UV radiation and humidity. The mechanical behaviour evidenced that the weathering process favoured chemical interactions between the fillers and the matrix polymer chains, enhancing the rigidity of the polymer matrix, especially in the case of LDPE/10LB.

REFERENCES

[1] I. Spiridon, *Cellulose Chem. Technol.*, **48**, 599 (2014).

[2] A. Treimanis, M. Laka, S. Hernyavskaya, J. Ganster, J. Erdmann *et al.*, *Cellulose Chem. Technol.*, **50**, 117 (2016).

[3] R. N. Darie, R. Bodirlau, C. A. Teaca, J. Macyszyn, M. Kozlowski *et al.*, *Int. J. Polym. Anal. Char.*, **18**, 315 (2013).

[4] R. N. Darie, M. Bercea, M. Kozlowski and I. Spiridon, *Cellulose Chem. Technol.*, **45**, 127 (2011).

[5] O. Faruk, A. K. Bledzki, H.-P. Fink and M. Sain, *Prog. Polym. Sci.*, **37**, 1552 (2012).

[6] I. Spiridon, K. Leluk, A. M. Resmerita and R. N. Darie, *Composites Part B*, **69**, 342 (2015).

[7] S. M. Mirmehdi, G. H. Denzin Tonoli and F. Dabbagh, *Cellulose Chem. Technol.*, **51**, 341 (2017).

[8] D. K. Setua, M. K. Sukla, V. Neegam, H. Singh and G. N. Mathur, *Polym. Compos.*, **21**, 988 (2000).

[9] A. F. M. Mirabella and A.A. Bafna, *J. Polym. Sci. Part B*, *Polym. Phys.*, **15**, 1637 (2002).

[10] K. A. Y. Koivu, H. Sadeghifar, P. Nousiainen, D. S. Argyropoulos and J. Sipila, *ACS Sustain. Chem. Eng.*, 4, 5238 (2016).

[11] P. Pérez-Guerrero, J. Lisperguer, J. Navarrete and D. Rodrigue, *BioResources*, **9**, 6514 (2014).

[12] J. L. Espinoza-Acosta, P. I. Torres-Chávez, B. Ramírez-Wong, C. M. López-Saiz and B. Montaño-Leyva, *BioResources*, **11**, 5452 (2016).

[13] R. Gadioli, W. R. Waldman and M. A. de Paoli, *J. Appl. Polym. Sci.*, **133**, 43558 (2016).

[14] I. Yakimets, D. Lai and M. Guigon, *Polym. Degrad. Stabil.*, **86**, 59 (2004).

[15] A. Duval and M. Lawoko, *React. Funct. Polym.*, **85**, 78 (2014).