EVALUATION OF PROPERTIES OF LDPE/OAK WOOD COMPOSITES EXPOSED TO ARTIFICIAL AGEING

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Due to their common use in outdoor applications, the durability of wood flour thermoplastic composites after ultraviolet exposure has become a special concern. Samples of 100% low-density polyethylene (LDPE) and LDPE filled with 10, 20, 30 wt% oak wood flour were melt-processed with a Brabender mixer and further weathered in an accelerated weathering chamber up to 500 h. The changes occurring in composites aged under controlled conditions were evaluated in comparison with the initial composites by measuring their mechanical properties and as well as by FT-IR spectroscopy. Melt processing was studied, while mechanical evaluation has been performed to follow composites behaviour on tensile and impact tests. The obtained results showed that, after accelerated weathering, the composites retain a higher fraction of the original mechanical properties. Fourier transform infrared spectroscopy (FT-IR) was used to monitor the changes of carbonyl and vinyl groups and dynamic rheology was used to evaluate the viscoelastic behaviour of the studied composites.

Keywords: oak wood composites, artificial ageing, FT-IR, mechanical properties, dynamic rheology

INTRODUCTION

The non-biodegradability of plastics, along with their disposal, has caused extensive environmental problems. Composites containing wood derivatives (WPC) have attracted a significant interest in the last decades, thanks to the specific advantages they can grant in comparison with the classic mineral filler/plastic composites.[1,2] These include mainly improved environmental performance, due to the use of biodegradable materials, and a lower use of non-renewable (oil based) resources throughout the whole life cycle of the composite. Significant interest has also been raised by the outdoor performance of these composites, in particular their resistance to photooxidation.

Wood particles with high strength and modulus – with good adhesion and uniform dispersion – can impart better mechanical properties to the host polymer, for obtaining a composite with better properties than those of the unfilled polymer.[3]

The presence of chromophores in plastics and wood usually enhances the absorption of ultraviolet (UV) light, causing subsequent WPC photodegradation. Photo-yellowing of weathered wood has been attributed to the breakdown of lignin into water-soluble products, eventually leading to the formation of chromophoric functional groups, such as carboxylic acids, quinones and hydroperoxy radicals.[4]

During polymer degradation, chain scission occurs *via* Norrish Type I and II reactions. Photochemical cleavage of aldehydes and ketones into free radical intermediates in the presence of UV radiation may occur *via* a Norrish Type I reaction. Norrish Type II reactions lead to the formation of carbonyl and vinyl groups. The effect of these reactions is a reduced density of chain entanglements in the amorphous phase, thereby allowing shorter molecules to crystallize, because of their higher mobility (lower entanglement).[5]

Consequently, the polymer properties, including melt flow/ viscosity, molecular weight and mechanical strength, are affected.[6]

The first key point for the production of acceptable WPC is the compatibility between wood and the host polymer matrix. Wood is hydrophilic in nature (high surface tension), which reduces its compatibility with the hydrophobic polymeric material (low surface tension) during composite preparation. To solve this problem, reactive functional groups may be incorporated into the synthetic polymer as compatibilizers, for enhancing the miscibility of the two polymers and for improving the overall mechanical properties of the blend. These reagents are compatible with the polymeric matrix and can also react with the hydroxyl groups of the fibre, forming covalent bonds. The modification of polyethylene (PE) should also provide increased polymer stiffness, while the PE should protect wood fibres against moisture absorption.

In this work, several composites were prepared from a polyethylene matrix and oak wood flour, by melt mixing and were subjected to accelerated UV weathering. The effects of exposure to UV radiation were studied by analyzing some mechanical properties. The photo-oxidation mechanisms of both polymer and filler were evaluated by FT-IR. The viscoelastic behaviour of the studied samples has been observed by dynamic rheology. This study is the first part of our on-going work on composites with oak wood and thermoplastic matrix, the next step being the obtaining and controlled ageing of compatibilized systems.

EXPERIMENTAL
Materials
The materials used in the study were LDPE and oak wood flour (W).

Low-density polyethylene (*LDPE*), A22FMA/002-type virgin material, with a melting temperature of 120 °C and a melt flow index of 0.3 g/10 min, was supplied by Petrom S.A., Romania. The filler – disperse sawdust (*oak wood flour*, *W*) was obtained from oak sawdust by grinding it in a high-speed chopper, screening through a sieve and drying for 17 h at 100 °C. Fractions screened through 0.25 mm mesh sieves were used in the experiments.

Preparation of composites
The composites were obtained by melt blending in a chamber of a Brabender mixer, at 145 °C. The systems were processed for 10 min at 60 rpm and their corresponding torque–time curves have been recorded during processing. Before mixing, the components were dried in a vacuum oven for 24 h at a temperature of 80 °C.

After the processing step, each sample was pre-melted for 5 min and then sandwiched in a Carver Press 4394, for 4 min, between two Teflon papers, and pressed at 145 °C under a pressure of 200 bars, to obtain the specimens for the mechanical tests. Three formulations were produced with LDPE as a matrix and various contents of oak wood (10, 20 and 30 wt%), as presented in Table 1.

Investigation methods
Weathering procedure
All composite samples were placed in a laboratory chamber (Angellantoni Ind., Italy), to accelerate sample weathering. The samples were exposed to the artificial light of a mercury lamp ($200 < \lambda < 700$ nm, incident light intensity – 39 mW cm^{-2}), at a temperature of 40 °C and humidity of 65%, while the exposure time was up to 500 h. The samples were removed from the chamber at regular intervals after 100, 200, 300, 400 and 500 h of exposure, then analyzed as to chemical changes and compared with the non-irradiated (reference) sample.

The processing behaviour was evaluated from the torque–time curves recorded during processing on the Brabender mixer.

Mechanical properties
Stress-strain measurements were performed at room temperature on dumbbell-shaped samples (1 mm thickness), on an Instron Single Column Systems tensile testing machine (model 3345) equipped with a 5kN load cell and activated grips, which prevented slippage of the sample before break, operated according to SR EN ISO 527:1996. The cross-head speed used was of 30 mm/min, and gauge length of 40.0 mm.

Impact tests have been performed according to SR EN ISO 179/2001, on a CEAST Impactor, equipped with a Charpy type hammer having 50 J energy.

Similarly with tensile tests, all unnotched samples were measured five times and the average was calculated.

FT-IR spectra
Infrared Spectroscopy (FT-IR) was applied with a VERTEX 7 Instrument equipped with a Golden Gate single reflection ATR accessory, spectrum range – 600-4000 cm^{-1}.

Dynamic rheological measurements
Oscillatory melt rheology tests have been realised on an Anton Paar rheometer equipped with CTD450, in plate-plate geometry, oscillatory mode, at a testing temperature of 145 °C.

RESULTS AND DISCUSSION
Compounding characteristics

Figure 1 presents the evolution of the mixing torque with blending time during processing. At a constant mixing speed, the variation in torque among samples at the same temperature is indicative of viscosity differences, viscosity being directly proportional to the ratio of torque and rotor speed.[7]

The analysis of the shape of the torque–time curves of the studied composites shows that the compounding of the LDPE/oak flour composites proceeded in several stages. During the first stage, the mixing torque sharply increased as LDPE or mixed LDPE/w was added. Simultaneously, the chamber temperature quickly decreased, due to feeding of cold materials. At a shorter time, the torque gets too high because of incomplete mixing and lack of equilibrium temperature. The torque decreases when the components start melting, because mixing becomes easier. Generally, the lower is the torque level, the less mechanical energy is necessary for processing a blend.

The presence of wood flour in blends affects the melt processing characteristics, which generally decrease when rising the oak wood content, the lowest torque *versus* time curve being recorded for a 30 wt% oak wood flour content in the LDPE matrix (P4). The lignin contained in oak wood acts as a plasticizer for these blends, improving the melting behaviour.

FT-IR spectroscopy

Polyethylene is a semi-crystalline polymer. Packing of the crystalline phase is much tighter than that of the amorphous phase and is impermeable to oxygen.[8] The degradation reactions therefore occur predominantly in the amorphous region, and are controlled by oxygen diffusion in this region.[9] While chain scission occurs in the amorphous phase of the polymer, UV-induced crosslinking occurs in the imperfect crystalline regions.[10,11]
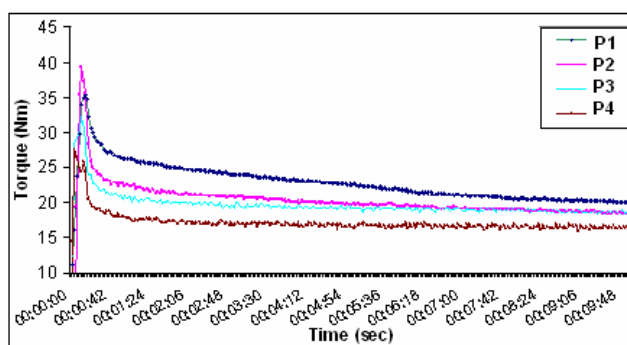

Figure 1: Torque–time curves of studied composites

Table 1
Blend composition, carbonyl and vinyl indexes for the reference (no UV) and the samples aged for 500 h under controlled conditions

Code	Sample	LDPE (%wt)	W (%wt)	Carbonyl index		Vinyl index	
				No UV	500 h	No UV	500 h
P1	LDPE	100	0	0.10	0.45	0.48	0.63
P2	LDPE/10w	90	10	0.25	0.27	0.46	0.32
P3	LDPE/20w	80	20	0.32	0.34	0.71	0.28
P4	LDPE/30w	70	30	0.34	0.37	0.52	0.23

FT-IR spectroscopy was used to check the occurrence of surface oxidation of the samples by investigating the carbonyl group change. In addition, the structural changes observed in the matrix after weathering were investigated by following the vinyl group formation in the composite samples.

Photodegradation of polyolefins is mainly caused by the introduction of chromophores, such as catalyst residues, hydroperoxide groups, carbonyl groups and double bonds, during polymer manufacture.[12]

Carbonyl groups are postulated to be the main light-absorbing species responsible for

the photochemically induced degradation reactions of UV-exposed polymers. The degradation reactions proceed from the carbonyl group precursors, according to Norrish type I and II reactions.[9,13] If degradation of the carbonyl groups proceeds according to the Norrish I reaction, the resultant free radicals can attack the polyolefin, which may lead to termination *via* crosslinking or chain scission. If degradation proceeds according to the Norrish II reaction, carbonyl and terminal vinyl groups are produced, and chain scission occurs. In addition, the carbonyl group formed is capable of further degradation. During accelerated polyethylene photodegradation, the two mechanisms, chain scission and crosslinking, compete.[14] Chain scission reduces molecular weight, whereas crosslinking raises molecular weight by increasing bonding between the polymer chains.

Ketones, carboxylic acids and vinyl groups are the three major functional groups accumulated with polyethylene photodegradation.[12,15]

Under irradiation, lignins – considered in the literature as the key structures involved in wood degradation – generate phenoxy radicals, while the phenols might be oxidized.[16,17] This effect is more and more prominent with increasing the amounts of wood within the composite. This can be explained by the radical species produced through wood photooxidation, which are likely to initiate the oxidation of the polymer, once the antioxidant has been consumed within the induction period. Consequently, wood acts as an initiator on the photooxidation of the polymer matrix in the composite material.

The FT-IR spectra plotted in Figure 2 evidence different bands, characteristic of the main components of the studied systems. Thus, the band at 1460 cm^{-1} is assigned to the CH$_3$ asymmetric stretch, CH$_2$ scissoring in lignin and to carbohydrates. The double band at 2850-2920 cm^{-1} corresponds to the methyl group region, while the band in the 3300-3900 cm^{-1} region is related to the OH and CH groups of wood stretching vibrations.

The formation of carboxylic acids occurs with chain scission, which is partly responsible for the formation of nano/microcracks on the surface of the

polymer, leading to the degradation of the material's mechanical properties.

The chemical modifications of the polymer, measured by the concentration of the oxidation photoproducts, can be quantitatively related to the mechanical degradation of the material.

Photooxidation rates

FT-IR spectroscopy was used to check the occurrence of surface oxidation of the samples through the investigation of a carbonyl group change. In addition, the structural changes produced in the matrix after weathering were investigated by observing vinyl group formation in both LDPE and P2-P4 composite samples.

The carbonyl index, as well as the vinyl index, have been calculated with the following equations:[12]

$$\text{Carbonyl index} = \frac{I_{1715}}{I_{2912}} \,(100)$$

$$\text{Vinyl index} = \frac{I_{908}}{I_{2912}} \,(100)$$

where I represents peak intensity. The peak intensities were normalized using the peak at 2912 cm^{-1}, which corresponds to alkane CH stretching vibrations of the methylene groups. This peak was selected as a reference, because it changed the least during weathering.

The increase in the carbonyl group concentration over the oak wood content in the studied samples during controlled ageing or under normal conditions is presented in Table 1. Under normal conditions, the carbonyl index increased for LDPE/oak wood composites (P2-P4), compared to that for the neat LDPE (P1). The addition of WF to the LDPE matrix increased the amount of oxygen in the sample, including carbonyl functionality.

As the exposure time increased to 500 h, the carbonyl index increased at approximately the same rate for the P2-P4 composite samples. An exception was found for the neat LDPE sample, where the carbonyl index registered the highest value, of ~0.45, four times higher than the value for LDPE under normal conditions. The increase in the carbonyl group formation for polyethylene after weathering is known to be proportional to the number of chain scissions occurring in polyethylene.[9] These results indicate that chain scission may have occurred upon exposure, and that the number

of chain scissions and, respectively, surface oxidation for LDPE-based wood composites increased at a 500 h exposure time.

Similarly with carbonyl group formation, vinyl group formation is indicative of polymer chain scission of either LDPE or oak wood, which can be a result of carbonyl degradation *via* Norrish II.[13] The values presented in Table 1 show the changes

observed in vinyl group concentration based on the peak at 908 cm^{-1}. Under normal conditions, the concentration of the vinyl groups is lower for the neat LDPE sample than that of the LDPE/wood composites (P3 and P4).
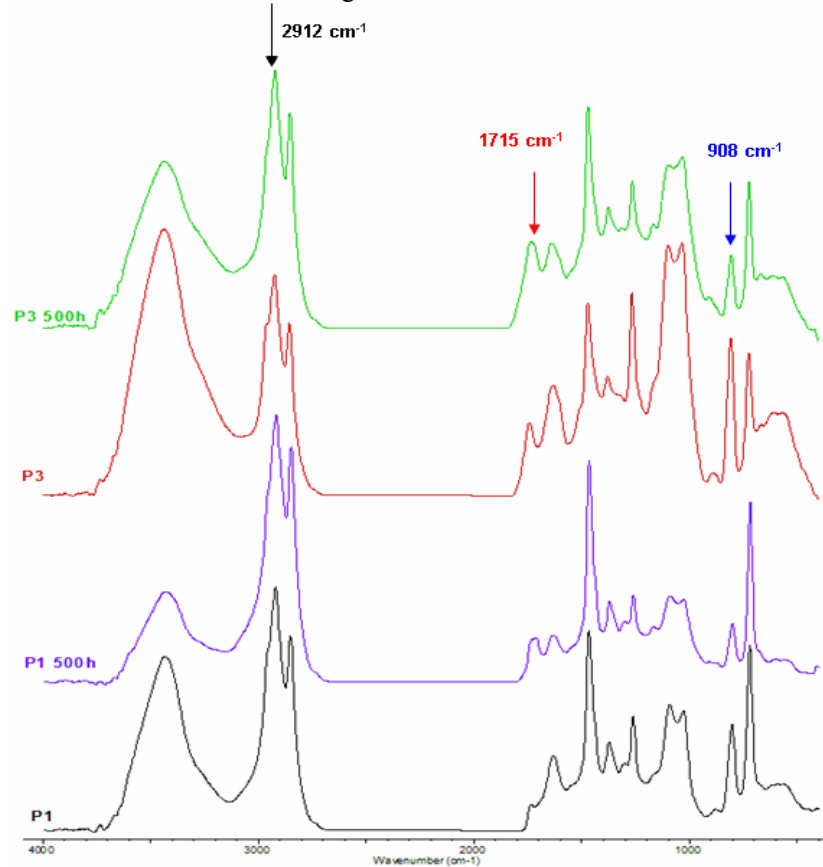
Figure 2: FT-IR spectra for P1, P3 systems before and after a 500 h exposure to controlled ageing

After 500 h, the vinyl index values of the LDPE sample significantly decreased with UV exposure time, a delay in vinyl group formation being observed in the weathered LDPE/wood flour (P2-P4). The change in vinyl group concentration is thought to be mainly due to the degradation of the LDPE matrix, as a component of LDPE/wood composites.

The energy of the H-bonds can be calculated with the following equation:[18]

$$EH (kcal) = 1/k [(vo - v)/vo] \quad (1)$$

where: vo – standard frequency corresponding to the free –OH groups (3650 cm^{-1}); v – frequency of the bonded –OH groups; $k = 1.68*10^{-2}$ kcal^{-1}.

The data presented in Table 2 indicate that the incorporation of oak wood particles into the LDPE matrix led to the

establishment of H bonds with a constant H-bond energy E_H, up to 20 wt% wood concentration. The higher wood concentration led to a slight decrease of the E_H value, which is probably due to the agglomeration of wood particles. The ageing process affects the sample surfaces, as reflected by the minor modification of H bond enthalpy, especially at a high content of oak wood (30 wt%), as due to the formation of polar groups under UV treatment conditions.

Mechanical properties of composites

Evaluating the results presented in Figure 3 one can observe that, compared to neat LDPE, the Young Modulus of composites increased with increasing the wood content in blends, as well as the time of exposure to

controlled ageing, especially for 30 wt%, stiffer materials being thus obtained. The PE matrix provides ductility, whereas the lignocellulosic flour exhibits brittle behaviour, with subsequent loss of toughness of the composite material.

It seems that, for LDPE, crystallinity increases or remains unchanged upon exposure to UV radiation. Cross-linking of LDPE competes with recrystallization, being an influential mode of photodegradation during accelerated weathering.

With a longer exposure time, the composites retained a higher percentage of the original mechanical properties, in comparison with the neat polymer, which may be explained if admitting that photooxidation involves only the surface of the exposed composite. The rigidity of composites increased compared to LDPE,

because of the chain scission reaction induced by irradiation. The effect of wood particles is even more pronounced for elongation at break, which decreases dramatically.

The composites containing oak wood recorded a decrease in impact strength, especially at a long exposure time, as shown in Figure 4. One may observe that the impact strength of the composites was less modified, compared to virgin LDPE, especially at a low concentration of wood flour. When 30% wood flour was added, the impact strength of the composite materials decreased. An irradiation time of 500 h mainly affected the composites with higher amounts of oak wood flour, wood degradation leading to the formation of chromophoric groups, which accelerate photooxidation and yellowing.

Table 2
Spectral characteristics of studied systems before and after a 500 h exposure to controlled ageing

Sample	υ_{OH} (cm^{-1})		Δ_{OH} (cm^{-1})		E_H (kcal)		ΔH (kcal/mole)	
	No UV	500 h	No UV	500 h	No UV	500 h	No UV	500 h
P1	3433.28	3429.43	581.01	537.97	3.53	3.59	9.93	9.24
P2	3433.28	3429.43	593.3	574.86	3.53	3.59	10.12	9.83
P3	3433.28	3431.36	667.08	645.56	3.53	3.56	11.30	10.96
P4	3439.07	3427.5	614.82	682.45	3.44	3.63	10.47	11.55

EH – H-bond energy; ΔH – H-bond forming enthalpy
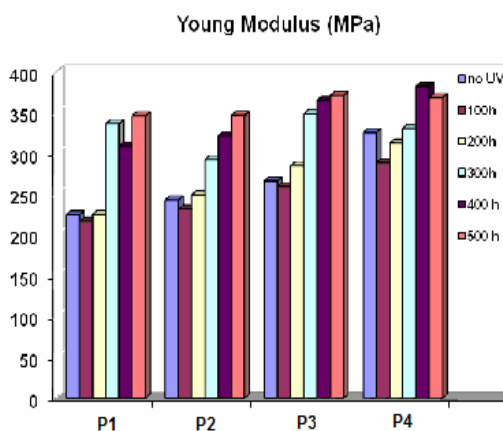
Figure 3: Young Modulus values plotted as a function of irradiation time and wood content

Figure 4: Influence of UV ageing on impact strength

The absence of a compatibilizer is remarked as the differences in the polarity of the main components led to low adhesion between the wood filler and matrix, and to poor stress transfer from the matrix to the filler, thus providing low impact strength to the P2-P4 composites. Lignocellulosic flour
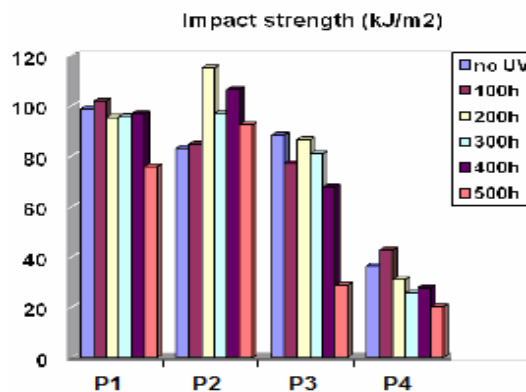
is responsible for the decrease in deformation capability. A further step in the investigation involves the incorporation of a maleated compatibilizer into P2-P4 composites, for enhancing both mechanical properties and ageing behaviour.

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Rheological properties

In oscillatory deformation tests, the measured complex shear modulus ($G*$) can be analyzed through its real and imaginary components, *i.e.*:

$$G*(t) = G'(t) + iG''(t)$$

where elastic (or storage) modulus G'' is a measure of the reversibly stored deformation energy, and the viscous (or loss) modulus G'' represents a measure of the irreversibly dissipated energy during a cycle.[19]

The loss factor, $tan\,\delta$:

$$tan\,\delta = \frac{G''}{G'}$$

is a dimensionless parameter associated with the degree of viscoelasticity of the sample, being a measure of the ratio of the lost energy to the stored energy in cyclic deformation.

The rheological behaviour of low-density polyethylene/oak wood flour composites was investigated in a melt state, for different amounts of wood particles, through oscillatory rheological tests, in the linear domain of viscoelasticity. A load applied to a reinforced composite material is transferred from the matrix to the filler by the shear stress along the filler–matrix interface. The viscoelastic parameters were analyzed as a function of the oscillation frequency, ω, at a constant temperature of 145 °C (Figure 5 a-b). It may be remarked that these parameters are affected by the presence of particles in the mixture; first, G' and G'' decrease with the concentration of wood flour from P1 (matrix) to P3 (20% wood), then G' slowly increases by further addition of wood, whereas the values of G'' for P3 are very close to those of P4.

For low ω values ($\omega < 0.5$ s^{-1}), the samples show a preponderantly viscous behaviour ($G'' > G'$) while, for high oscillation frequency, all samples show a preponderant elastic behaviour ($G' > G''$) (Figure 6). From crossover frequency (ω_i), the relaxation time (θ) can be calculated as $\theta = 1/\omega_i$. The ω_i and θ values obtained for the P1-P4 samples are given in Table 3. The relaxation time increases with increasing the oak wood flour amount.

The plot of the loss tangent presented in Figure 7 shows the same differences among various samples only for low ω values. For a high oscillation frequency, the ratio between the viscous and the elastic character is nearly the same for all samples.

Table 3
Crossover frequency (ω_i) and relaxation time (θ) values for P1-P4 systems

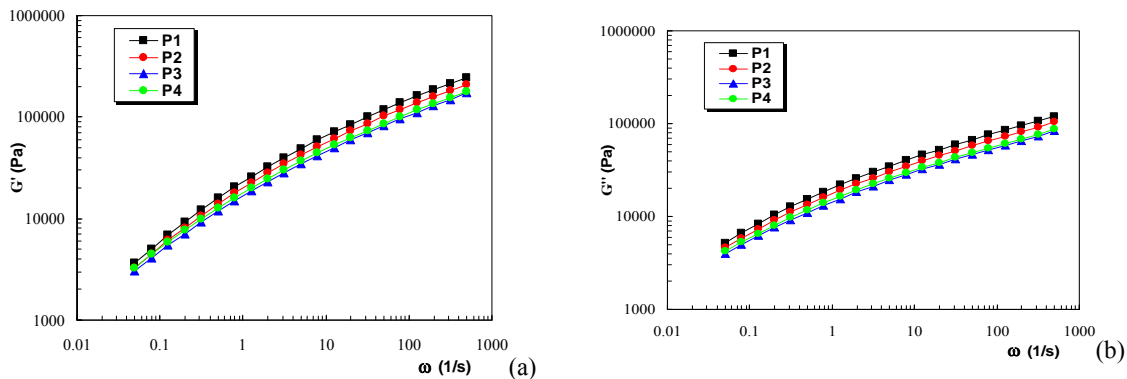| Sample	Cross over frequency, ω_i (s^{-1})	Relaxation time, θ (s)
P1	0.43	2.35
P2	0.40	2.53
P3	0.32	3.17
P4	0.27	3.77

Figure 5: Viscoelastic parameters (a) storage modulus and (b) loss modulus, as a function of oscillation frequency, ω, at 145°
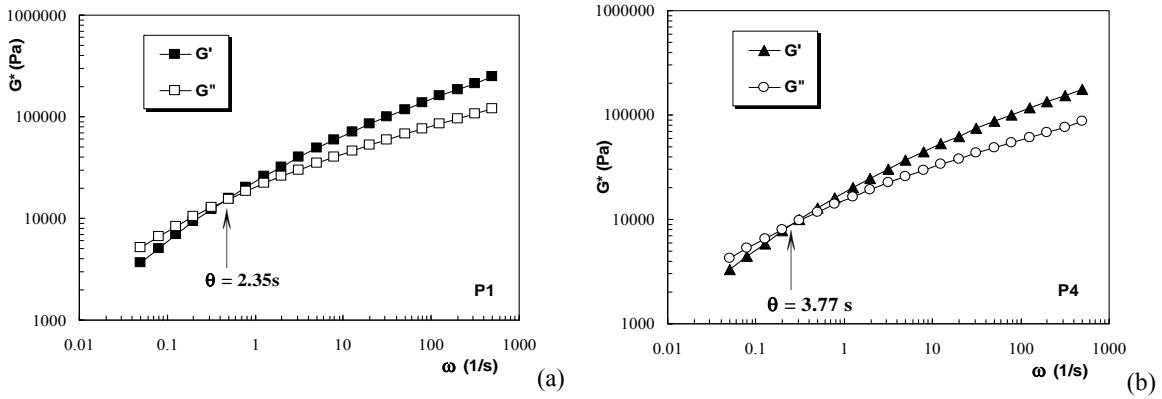
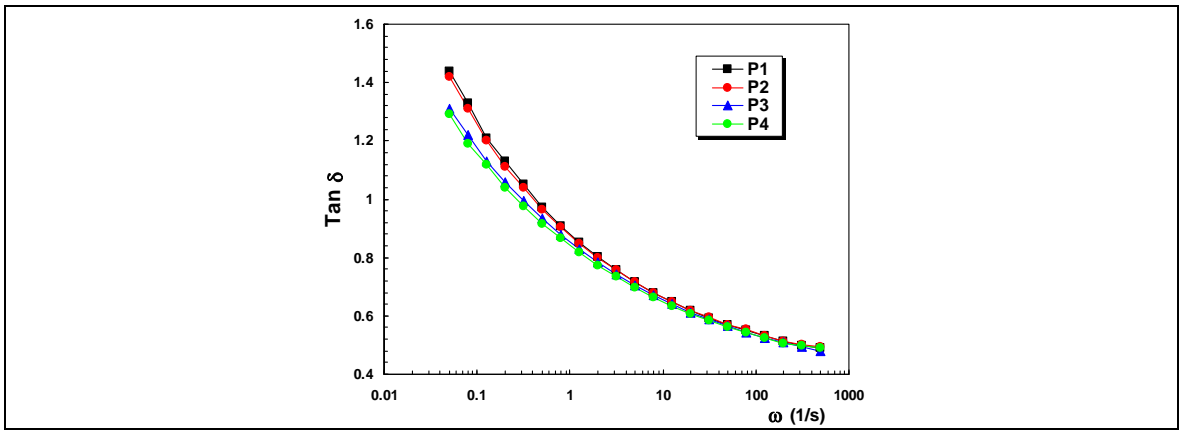Figure 6: Correlation between viscous and elastic behaviours for studied composites

Figure 7: Variation of loss tangent corresponding to P1-P4 systems as a function of oscillation frequency
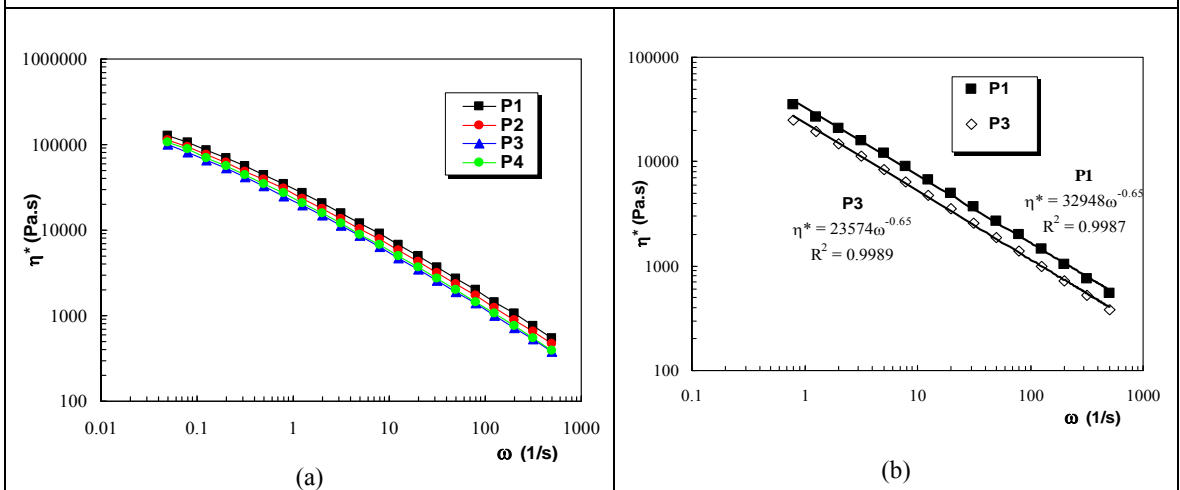

Figure 8: Variation of complex viscosity with angular frequency for untreated P1-P4 composites

In the investigated range of oscillation frequency, all samples show a pseudoplastic behaviour, as it may be observed from the dependence of complex viscosity, η*, as a function of angular frequency (Figure 8a). This shear thinning behaviour has been attributed to the disruption of the initial structure of the filler in LDPE melts.

Complex viscosity varies as $\omega^{-0.65}$ for the matrix (P1), as well as for the blends containing different amounts of wood flour (Figure 8b), the presence of additive in the polymer matrix inducing no change in the viscosity dependence on the shear conditions. The composites filled with oak flour exhibited decreased melt viscosity

compared to the matrix, the reason being related to the fact that lignin acts as a plastifier and reduces the resistance of the matrix to the external forces, determining an improvement of flow for reinforced systems.

CONCLUSIONS

Low-density polyethylene/oak wood flour composites were prepared by melt mixing, and their behaviour upon controlled weathering was investigated.

The mechanical tests showed that, after accelerated weathering, the composites retained a higher fraction of the original mechanical properties. The stabilizing effect of wood flour could be explained by the possible action of the filler as a "screen", confining photodegradation to the outer layers of the samples.

FT-IR spectroscopy evidenced carbonyl and vinyl group formation during weathering. An increase in the calculated carbonyl index denotes an increase in polymer chain scission. The change in vinyl group concentration is thought to be mainly due to the degradation of the LDPE matrix, as a component of the LDPE/wood composites.

The composites with 10-30 wt% wood loading levels behaved as pseudoplastic materials. By increasing wood addition, the amount of plastics in the composite is reduced, and the overall effect on the durability of the composite material might be considered positive, if one considers the degradation level of the composite and that of the pure polymer after the same ageing time.

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