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Easy estimation of the progress of artificial weathering of palm fiber-polypropylene composites by chemiluminescence

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Date palm leaves were compounded with polypropylene (PP) and UV stabilizers to form composite materials. Residual thermo-oxidation stability of such composites undergone to accelerated weathering in Xenotest has been investigated by chemiluminescence method. It has been found that composites are much more stable than PP alone which was attributed to the direct interaction of cellulose fibres (reinforcing effect) and lignin (anti-oxidation effect) with polypropylene peroxyl radicals. Samples in which polypropylene is compatibilized with cellulose by Epolene E-43 wax are generally less stable than uncompatibilized ones probably because of the pro-initiation effect of cellulose on polypropylene oxidation. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Since 1990 one can register an increasing interest in the development of industrial and consumer products that combine lignocellulosic fibers and plastics. The primary impetus has come from one of these goals:

1. To reduce material costs by combining a lower cost material acting as filler or extender with a higher cost material [1–3].
2. To develop products that can utilize recycled materials.
3. To produce a composite material that exhibits specific properties that are superior compared to either of the component materials alone (e.g. increased strength to weight ratio, improved abrasion resistance, etc.) [4].

The processing temperature of thermoplastics with cellulosic fibers is limited due to the cellulose degradation at higher temperatures. However, it has been reported that no deterioration of properties of composite materials containing cellulose was observed when processing temperatures are maintained below 200°C [5].

The composites of cellulose fibers with thermoplastics can withstand higher stresses than either their individual constituent because the fibers and matrix interact and redistribute the stresses. The ability of these two constituents to exchange stresses depends critically on the effectiveness of the coupling or bonding between fiber and matrix [6]. It is well known that compatibility between lignocellulosic materials and the polymer matrix plays a crucial role in determining the properties of a composite. Lignocellulosic materials, which have polar hydroxyl groups on the surface, have difficulty in forming well bonded interfaces with non polar polymer matrix materials such as polyethylene and polypropylene [7–10]. Various chemical reagents have been employed to enhance the compatibility between the constituent materials. These include Epolene E-43 (Maleic anhydride modified polypropylene) [2, 7, 8, 11–13], poly[methylene(polyphenyl isocyanate)] (PMPPIC), γ-methacryloxypropyltrimethoxysilane, poly(propylene acrylic acid) and poly(propylene-ethylene acrylic acid) [7], etc.

From the practical viewpoint, the resistance of the above materials towards thermo-oxidation should be of interest as it determines the remaining service life of the material. Until now very few studies investigating the artificial weathering of polypropylene/cellulose fiber composites exist. On the other hand, the antioxidant properties of lignin in polypropylene were reported several times [14–16]. The authors underline the necessity of compatibilization of lignin with polypropylene to explore the maximum of its antioxidant properties due to hydroxyl groups involved in monomer unit.

Objective of this report is to show how the extent of stabilization of polypropylene/date palm cellulose fiber composites changes with the time of exposition of sample to artificial ageing. The chemiluminescence method has been used for an easy characterization of the remaining thermo-oxidation stability.

The thermal oxidation of polypropylene alone was examined by this method many times and the agreement between induction time so determined and those determined by other methods was several times reported. The method itself is typical with extreme sensitivity but the chemiluminescence behavior of polymers may differ each from the other. There are polymers, polypropylene including, which give typical sigmoidal autocatalytic increase of the light emission under isothermal conditions which coincides with the oxidation runs determined by other methods. On the other hand, cellulose has a relatively short length of kinetic oxidation chains and does not give an autocatalytic shape of chemiluminescence runs. Intensity of the light emission of oxidized cellulose decays steadily from the initial level. Different authors [17–26] indicate that the elementary processes from the oxidation mechanism which might be responsible for the light emission are not quite clear but the predominating opinions favor the recombination of peroxyl radicals which proceeds according to Russel's scheme.

$$2R_1(R_2)\mathrm{CHO}_2^{\cdot} \rightarrow \mathrm{O}_2^{*} + R_1(R_2)\mathrm{CHOH} + R_1(R_2)\mathrm{C} = \mathrm{O}^{*} \qquad (1)$$

In the Equation 1 asterix denotes the excited singlet state of oxygen and excited triplet state of carbonyl groups on the polymer chain, respectively. The light comes from the transfer of these excited particles to their ground states. Together with this emissive route of deactivation of excited states there occur quenching processes. Non-emissive way of transfer of excited into ground state may be much more significant and may modulate the proportionality constant Φ in linear relation between chemiluminescence intensity I and the rate of oxidation.

$$I = \Phi \cdot \text{rate of oxidation} \qquad (2)$$

2. Experimental

2.1. Materials

Polypropylene used in the study was supplied by Saudi Basic Industries Corporation (SABIC). The brand name for it is LADENE PP570P. It is a homopolymer used for producing rigid injection molded articles. Details of the polymer are given in Table I. Maleated polypropylene (Epolene E-43) was used as a compatibilizer and was supplied by Eastman Chemicals (Kingsport, TN). Two stabilizers Irgastab and Tinuvin-783 (CIBA, Switzerland) were used to stabilize the composites for thermal and UV degradation during processing and weathering. Polypropylene wax was added to facilitate the injection molding of the composites. The formulations used in preparation of composites are shown in Table I.

TABLE I Formulation of composite dumb-belled shape injection molded test specimen

Sample identification	Formulation	
PP-1	PP (Sabic Laden-570 P):	68.11%
	Fibers:	29.19%
	Wax:	2%
	Irgastab FS 410 FF:	0.2%
	Tinuvin-783 (UVS):	0.5%
PP-2	PP (Sabic Laden-570 P):	63.91%
	Fibers (local dates tree leaves):	27.39%
	Wax Paraffin M. P. plasticized p:	2%
	Irgastab FS 410 FF (Ciba):	0.2%
	UVS Tinuvin 783 (Ciba)	0.5%
	Compatibilizer Epolene E-43 Wax (Eastman):	6%

2.2. Fiber preparation

Branches obtained from palm trees were cut into pieces about 6 inch long. Thereafter, they were air dried for 48 h at room temperature. The pieces of branches were then granulated to a small size using a Granulator (Rapid Granulator Inc, USA, Type 79-C, No. 201544). The fibers were then size separated by using sieving machine. Only the large fraction of fibers was used in this study. The fibers size distribution was characterized using a digital vernier caliper. The average length of the fibers was 4.7 mm with a standard deviation of 1.7 mm and an aspect ratio of 10.8. The fibers obtained were then cleaned to remove the volatile organic compounds. The chemicals used for cleaning were Ethanol and Toluene in the ratio of (1:2) (V/V). The mixture of these two chemicals was prepared in a large container. The fibers were soaked in the mixture for 24 h. The fibers were then washed with water and dried in a vacuum oven (Blue M Electric Company, Model OV-490A-2) at 105°C for 24 h to remove residual moisture.

2.3. Compounding and molding

The composite components were compounded using a Brabender Measuring Head, Model S-650, No:G126 mounted with a single screw extruder. The fibers were hand mixed with polypropylene and other additives prior to compounding. In both cases the fibers and the resins were first hand mixed in a bowl and then transferred to the mixer/extruder. The conditions of mixing were varied in such a way to determine the optimum conditions that will produce samples with maximum dispersion of fibers, good mechanical properties, good color and smell. The mixed composites obtained from the extruder were granulated then molded using an injection molding machine (Engel Electronics Model ES 80/25, Guelph, Canada) at 200°C. The composite specimen were molded into standard ASTM D-648–94B specimen, which were then weathered and characterized.

2.4. Weathering trials

The complete details of the trials may be seen below:

Equipment used:	Xenotest Beta-LM
Total duration of exposure:	2000 h

Parameters of Xenotest Beta-LM (as per ASTM D-2565):

• Irradiance:	45 w/m^2 between 300–400 nm
• Black panel temp. (BPT):	63° ± 3°C
• Black sensor temp. (BST):	70° ± 3°C
• Humidity:	50 ± 5%

2.5. Characterization of aged samples

The composite materials exposed to artificial weathering trials were characterized by mechanical testing parameter such as stress at break. The samples were tested using an Instron 5560 Mechanical Testing Machine. The tests were conducted at a constant strain rate of 2 mm/min. The measured quantity was the stress at maximum load in MPa. The melting temperatures of the samples were characterized using a Perkin Elmer DSC instrument. 10 mg samples were used for the tests. The temperature range of each scan was 50–190°C and the heating and cooling rates were 10°C/min.

2.6. Chemiluminescence measurements

Chemiluminescence experiments were performed on the photon counting instrument Lumipol 3 manufactured by the Polymer Institute of Slovak Academy of Sciences, Bratislava, Slovakia. The instrument dark count rate was 2–4 counts/s at 40°C. The measurements were carried out in an oxygen flow of 3 L/h.

Polymer composite samples for chemiluminescence measurements were cut by microtome knife from standard samples for mechanical testing and placed into aluminium pans. The average weight of the samples was 12 mg. Isothermal CL runs were performed at temperatures between 140 and 180°C. Non-isothermal runs were performed so that the sample was kept at 40°C for 10 minutes, then temperature started to increase by the rate of heating 2.5°C min^{-1} till 200°C and cooled subsequently by the same rate to 180°C. At this temperature measurement continued as an isotherm.

3. Results and discussion

Fig. 1 shows two cases of the chemiluminescence intensity runs in time provided that temperature of the sample changes according to the program described by the dotted line. The residual stability of more aged samples was lower and chemiluminescence light emission started to increase earlier. At the same time, the maximum intensity at 200°C is higher for aged sample. For unaged and thus the most stabilized PP-2 sample there may be observed some induction period when continuing with isothermal heating at 180°C after the nonisothermal run from 40 to 200°C. This is not the case for the aged sample (see e.g. the case after 1600 h of ageing) where a sharp increase of the CL intensity is observed already during nonisothermal temperature ramping (Fig. 1).

The whole set of experiments of artificially aged samples may be seen in the Fig. 2. The residual stability of the aged samples is dependent on the time of ageing exposure. The higher the time of sample ageing, the more significant shift of the chemiluminescence signal towards lower temperatures occurs.

Quite of interest is comparison of isothermal experiments at temperatures between 140 and 180°C (Fig. 3). Several zones may be observed on isothermal runs. First (I) is typical by a steady decay of chemiluminescence intensity, the second (II) characterizes the end of induction period, where chemiluminescence intensity starts to increase, the third (III) is the region of the maximum light emission and the fourth (IV) is accompanied by the new emission decay. The surprising observation has been done, namely that the induction period of oxidation which is well observable for pure polypropylene (Fig. 4) cannot be observed at 140°C and lower temperatures. As it is seen in the Fig. 3, a considerable increase of CL signal for composite materials and thus well distinguished induction period of oxidation may be seen above 170°C, only when polypropylene melts and the mobility of the macromolecular chains becomes released. One can see the large difference between runs of chemiluminescence signal of PP-2 aged 2000 h and measured at 170 and 180°C in oxygen. The increase of temperature from 170 to 180°C brings about here more than 10 times stronger maximum chemiluminescence signal, while the corresponding ratio between 170 and 160°C is about 3, approximately. The reinforcing effect of cellulose fibers seems to be from that quite evident. Palm leaves fibers reduce the mobility of

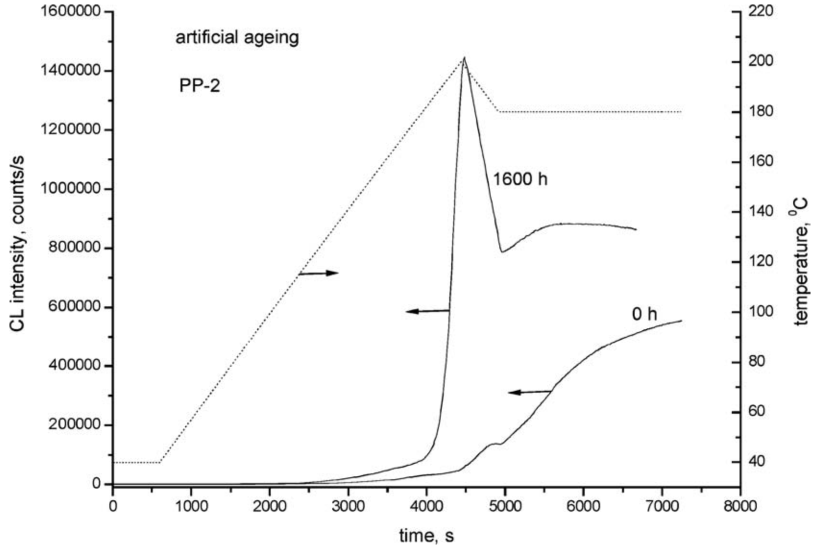

Figure 1 The comparison of residual stability of artificially aged composites of PP-2 determined by chemiluminescence in oxygen. The temperature program may be seen from dashed line.

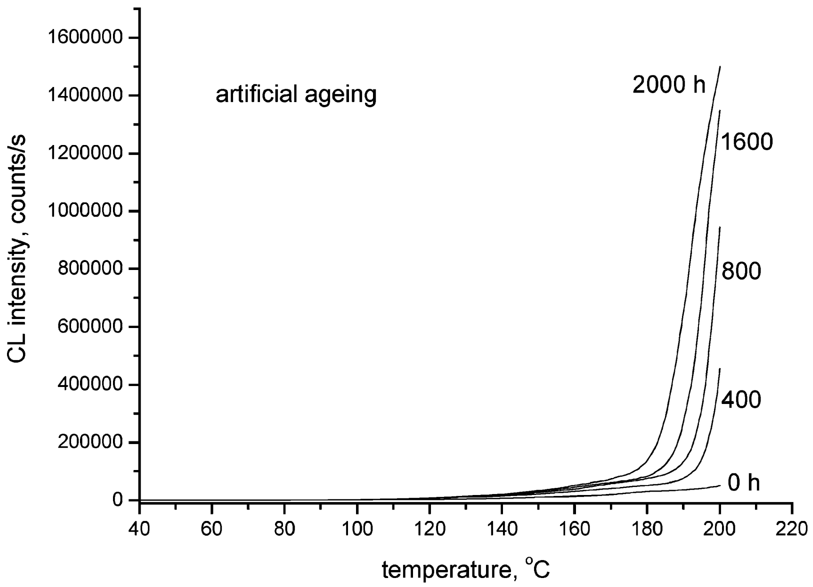

Figure 2 Nonisothermal chemiluminescence runs for artificially aged samples (0, 400, 800, 1600 and 2000 h) PP-2. The rate of the sample heating was 2.5°C/min.

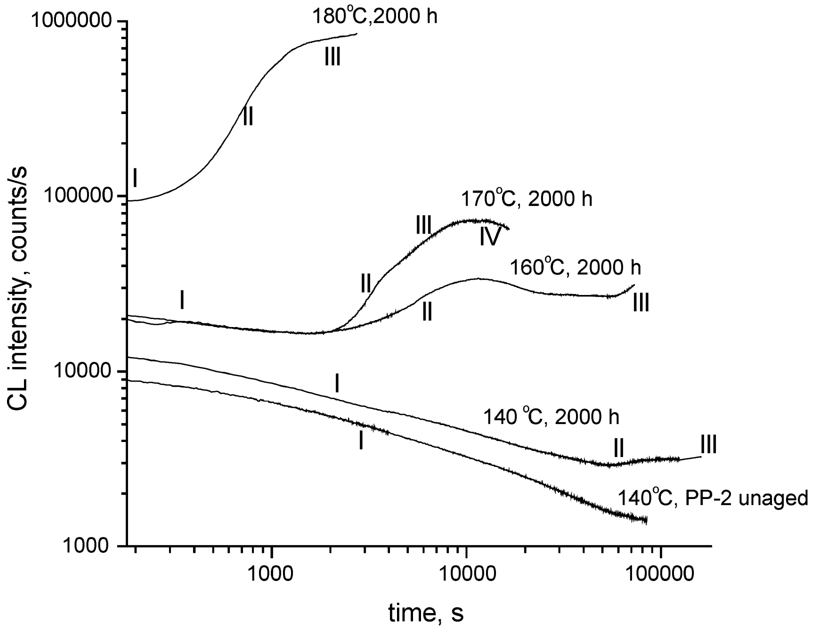

Figure 3 Isothermal chemiluminescence runs in oxygen for compatibilized polypropylene composites PP-2 with palm leaves.

the polypropylene chains when compared to polypropylene alone and it is quite possible that the mechanism of chemiluminescence changes, too. We remind here that both Irgastab 410 and Tinuvin 783 used in our experiments are very weak antioxidants and that their effect on prolongation of induction time is negligible under the conditions of thermo-oxidation experiments.

The compatibilized samples PP-2 are less stable than uncompatibilized PP-1. This is seen in Fig. 5 where PP-1 and PP-2 are compared after 400 h of ageing. This result is somewhat surprising; in compatibilized samples the contact of hydroxyl groups from cellulose and/or lignin is definitely better than in uncompatibilized ones and one should expect that compatibilization has to lead to a better stabilization of the composite. The explanation of such a contradiction may consist in pro-initiation effect of cellulose itself. Its monomer unit contains 5 tertiary carbon atoms which are rather susceptible to the direct interaction with oxygen which subsequently leads to free radical process. The compatibilizer is likely to facilitate the transfer reaction of hydrogen peroxyl radicals or peroxyl radicals formed in cellulose bacbone with polypropylene tertiary carbons and oxidation of polypropylene may thus be more pronounced.

From Arrhenius plots of chemiluminescence intensity on temperature, the breaking points may be found at which the oxidation passes from the region of lower activation energy characterized by a lower slope to accelerated region of oxidation where the chemiluminescence increase is determined by the chain reaction of accumulating hydroperoxides (Fig. 6). It is of interest that the lower slopes correspond to activation energy between 50–70 kJ/mol, while those at accelerating

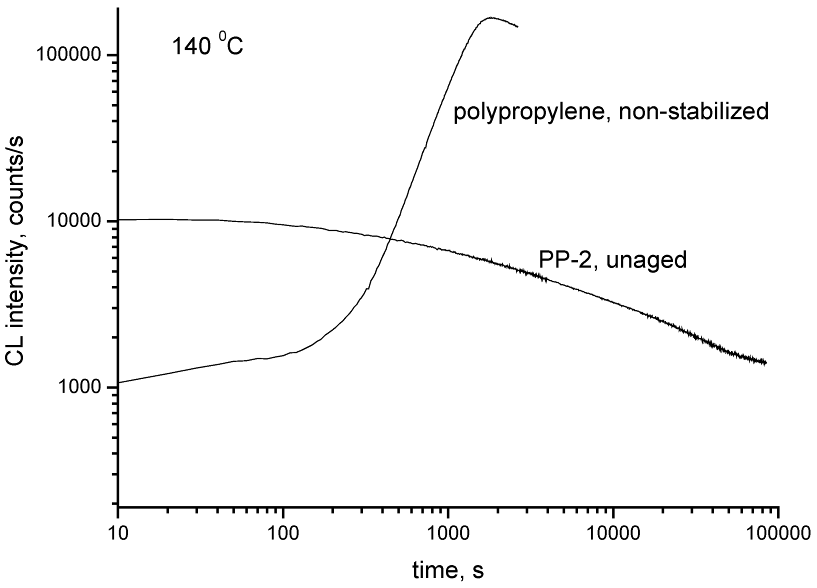

Figure 4 Isothermal oxidation runs for polypropylene samples, oxygen.

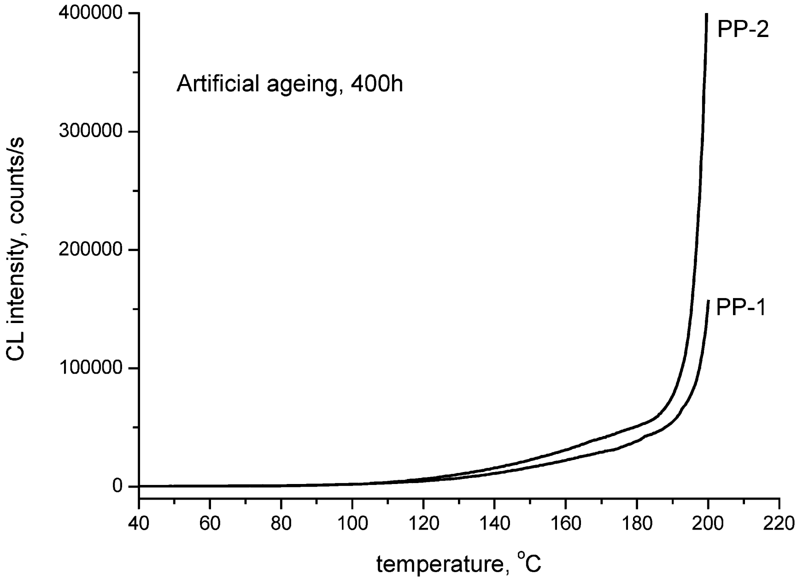

Figure 5 Comparison of non-isothermal oxidation runs for uncompatibilized (PP-1) and compatibilized (PP-2) polypropylene composites in oxygen, the rate of heating 2.5°C/min.

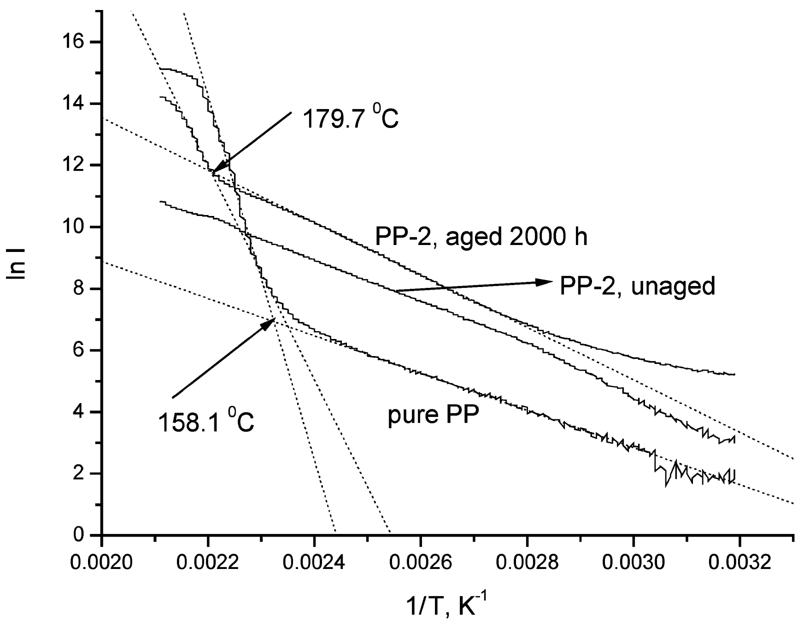

Figure 6 Arrhenius coordinates for non-isothermal chedmiluminescence runs of several polypropylene samples.

region are higher than 200 kJ/mol. The temperatures corresponding to the breaking points decrease with the time of sample ageing indicating again a lower residual stability of artificially aged composite when compared with non-aged samples.

Which is the reason of a low activation energy for the first stages of non-isothermal oxidation run? The answer may follow from the Fig. 4 where the decay of chemiluminescence intensity was observed for unaged sample PP-2 for time as long as 100 000 s. When oxidation process is in the region of induction period and the heating takes place with linearly increasing temperature, the corresponding chemiluminescence response is composed from two parts. The first which corresponds to the kinetics of the light emission decay (region I in Fig. 3) which is superposed with the increase (region II and III in Fig. 3). In non-isothermal experiments this ultimately leads to a lower activation energy of chemiluminescence increase when compared with the situation after induction period.

Melting temperatures of the artificially aged samples decrease with time of ageing as well. The melting temperature of PP alone dropped sharply from 164 to 138°C already after 800 h of exposure; then it continued to decrease at a slower rate. The uncompatibilized and compatibilized samples showed similar tendencies in stabilities and their melting temperatures showing only a 5% drop (Fig. 7). The correspondence with the temperature of the start of oxidation in non-isothermal chemiluminescence tests is quite evident.

The stress at maximum load of the artificially aged samples for both the compatibilized and uncompatibilized samples indicates also much higher stabilities than the PP without any cellulose fiber. The drop in the strength does not exceed 20% after 2000 h of ageing exposure (Fig. 8). The PP alone shows a slight decrease

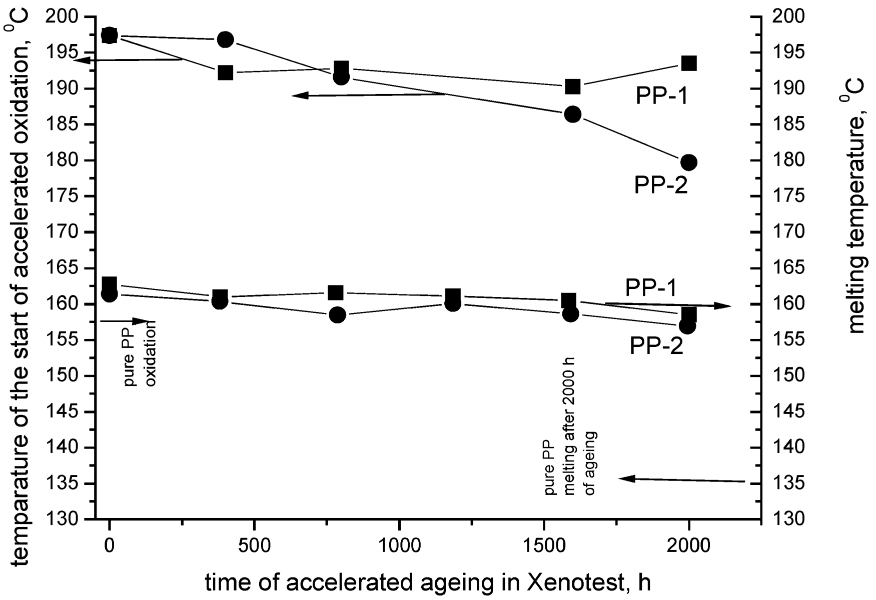

Figure 7 Correlation of the temperature of the start of accelerated oxidation and melting temperatures with time of accelerated ageing in Xenotest.

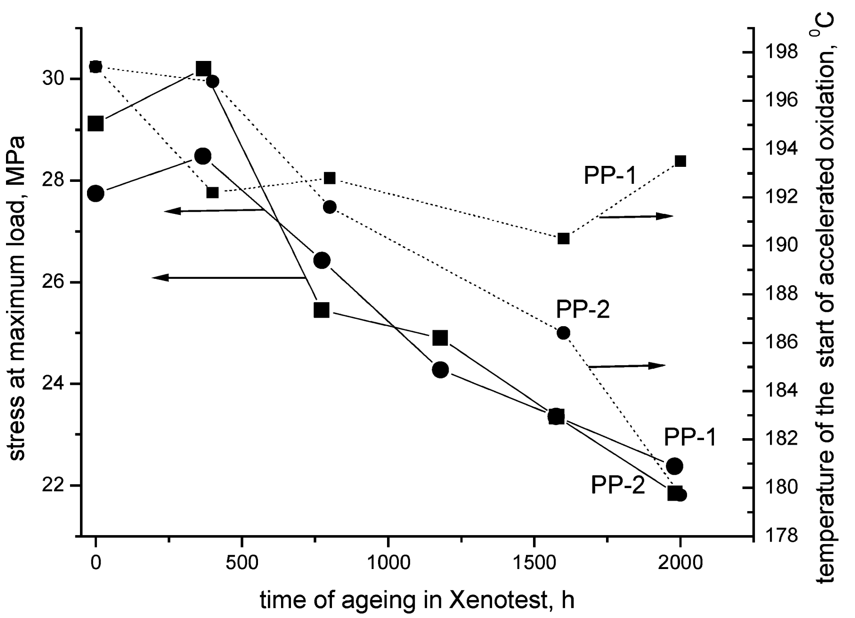

Figure 8 Correlation of the stress at maximum load and the temperature of the start of accelerated oxidation with time of ageing in Xenotest.

in strength in the first 500 h of exposure followed by a sharper drop. After 2000 h of exposure, the PP alone loses 85% of its strength. The fast rate of degradation in the accelerated ageing might offset any enhancement in interfacial adhesion caused by degradation and as a consequence, no increase in strength is observed.

4. Conclusions

PP/date palm cellulose fiber composites are found to be much more stable towards thermal oxidation than polypropylene alone while the continuous accelerated weathering reduces the thermo-oxidation stability according to the extent of ageing. Compatibilized samples are generally less stable than uncompatibilized ones. This may be the result of an complementary initiation of oxidation coming from cellulose itself. In addition to enhanced stability imparted by presence of the fibers in the composites, enhanced interfacial adhesion resulting from oxidation of the polymer matrix can be the source of retention of mechanical strength. The progress of the sample degradation due to artificial weathering may be easy estimated by non-isothermal chemiluminescence runs. The samples which are more degraded are shifted distinctly to lower temperatures.

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