

Conversion of Plastic/Cellulose Waste into Composites. II. Improving Adhesion Between Polyethylene and Cellulose Using Ozone

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SYNOPSIS

The effect of ozone gas treatment on the adhesion between low-density polyethylene (LDPE) and cellulose was investigated. The ozone treatment of LDPE resulted in a significant increase in the interfacial shear strength as measured by the single fiber fragmentation test, whereas the ozone treatment of cellulose was not successful in improving the adhesion. An extensive surface characterization was performed to elucidate the adhesion mechanism using ESCA, ATR-FTIR, contact angle measurements and iodometry. Among the species formed during the ozone treatment were several different carbonylic compounds, as well as hydroperoxides. The polar component of the surface energy increased for the ozone-treated materials as a result of the oxidation. Extraction of LDPE laminated with a regenerated cellulose film showed that strong bonding is achieved between the ozone-treated LDPE and cellulose during the lamination procedure. The suggestion proposed here for the adhesion mechanism is based on interactions between oxygen-containing species in both materials and the formation of covalent bonds originating from the decomposition of hydroperoxides. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The addition of cellulose fibers to thermoplastics can yield composite materials with increased strength and stiffness.^{1,2} However, in many cases, enhancing composite strength using cellulose fibers requires surface modification of one of the components, owing to the lack of interaction between cellulose and many thermoplastics.^{3,4} The addition of chemical compatibilizers and the use of treatments that can introduce oxygen-bearing moieties on the surfaces (plasma, corona, and ozone) are among the techniques that have been employed to increase the interaction and adhesion between the materials.^{2,5-8}

Enhancing the performance of plastic/cellulose materials using surface treatment is not limited to laminates and composites based on virgin materials. The potential for recycling and the conversion of

mingled plastic/paper waste into more valuable products are largely dependent on the improvement of mechanical properties of such materials. Hence, the mechanical performance of recycled materials must be acceptable and the price of such recycled products be kept low to be competitive with virgin materials. A simple, cheap, and efficient route for achieving materials with good properties is thus required.

Ozone treatment is a method that has been proven to oxidize many surfaces and has been proposed to be active in enhancing adhesion between materials. However, little work has been done on the actual adhesion mechanism between ozone-treated materials.^{7,9} The goal of this investigation was thus to evaluate the effect of ozone gas treatment on the adhesion between two common components in mingled waste: low-density polyethylene and cellulose. This study utilized regenerated cellulose in the form of fibers, membranes and films as a model for cellulosic materials in general, such as paper, board etc.

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EXPERIMENTAL

Materials

Low-density polyethylene (LDPE), NCPE 1800, with no additives according to the supplier Borealis AB, Stenungsund, Sweden. Specific gravity: 0.921 g/cm³. MFR: 2 g/10 min. (ASTM D1238).

Three different types of regenerated cellulose were used in the study owing to the experimental techniques utilized: fibers, membranes and films. The fibers were supplied by Svenska Rayon AB, Sweden, and had an average fiber length of 40 mm, a diameter of 12 μm , and a specific gravity of 1.59 g/cm³. The membrane filters had an average pore diameter of 0.2 μm and came from Schleicher & Schuell, Germany (RC58). The specific surface area of the membrane filter was $16.62 \pm 0.46 \text{ m}^2/\text{g}$ as determined by BET measurements. Courtaulds supplied the cellophane designated 350P00, which was used as film material. All cellulosic materials were first cleaned in boiling water for 12 h and then soxhlet-extracted with dichloromethane for a further 12 h. The molecular weight was determined by size exclusion chromatography (SEC) for LDPE and by a capillary viscosimeter for cellulose, using a standard procedure Scan-C 15 : 62.¹⁰ The strengths of the materials were determined with an Instron 1122 tensile testing machine. The speed was set to 5 mm/min and the test was performed at 23°C ($\pm 0.5^\circ\text{C}$) and 50% ($\pm 2\%$) relative humidity.

Ozone Reactor

Treatment of the materials took place in the ozone reactor described below. Oxygen gas (250 dm³/h) passes the ozone generator, which creates an ozone/oxygen mixture by an electrical discharge. The outlet from the generator contains 25 g of ozone/m³ total volume gas (NTP) as measured by an ozone meter. The ozone/oxygen mixture is then passed through a water seal, which humidifies the gas to about 80% relative humidity. The samples are mounted in small glass tubes which the gas stream passes by when the tubes are fitted into the reactor. The temperature in the reactor is maintained at 30°C.

Surface Characterization

Characterization of the surface chemistry of the materials was performed using ESCA, FTIR, DCA, SEM and the iodide method. An AEI ES200 Spectrometer was used for the Electron Scattering for Chemical Analysis (ESCA) spectrum. Fourier

Transform Infrared Spectroscopy was performed on the surfaces of the materials using a KRS-5 crystal and the Attenuated Total Reflectance (ATR-FTIR) technique. The Perkin Elmer FTIR System 2000, equipped with an MCT detector, was used to accomplish 250 scans on each surface.

The surface energy of LDPE films and regenerated cellulose fibers was analyzed using a Cahn Dynamic Contact Angle (DCA) Analyzer. The distilled water used had a resistivity of 1 Ωcm^{-1} and all other solvents were of p.a. quality. The speed of immersion was 19.6 $\mu\text{m}/\text{min}$. The polar and dispersive components of the surface energy were calculated using the harmonic mean equation and the measured contact angles of diiodomethane and water on LDPE films and regenerated cellulose fibers.¹¹ The acid-base work of adhesion was determined following the procedure described by Vrbanac and Berg.¹²

The "iodide method" was used for determination of hydroperoxides on the surface, as proposed by Carlsson and Wiles.¹³ The absorbance of the solution was recorded at 360 nm using an ultraviolet spectrophotometer Perkin Elmer 554. The extinction coefficient was set to 25,000 cm^{-1} .

The appearance of the surfaces was investigated using a Scanning Electron Microscope (SEM) Zeiss DSM 940A, operated at 20 kV.

The Single Fiber Fragmentation Test

Samples for the single-fiber fragmentation (SFF) test were prepared by the following procedure: Single regenerated fibers were placed between two LDPE sheets. The sample was pressed at 140°C for 2 min, holding no pressure during the first and applying about 8 MPa during the second minute. Pressed films were immediately placed between two aluminum plates (10 mm thick, 1.2 kg each) to ensure uniform cooling from melt. Dogbone-shaped specimens with a single fiber, aligned in the direction of elongation, were punched out from the film. The procedure for evaluation of interfacial shear strength using the SFF test was followed as described elsewhere.¹⁴ At least 150 fragments/treatment were used for the evaluation of the critical fiber length as a measurement of adhesion. A normal distribution of fragments was assumed owing to lack of fit to the Weibull model distribution.

RESULTS AND DISCUSSION

The Interfacial Adhesion

The interfacial adhesion between LDPE and regenerated cellulose fibers, as measured by the SFF test,

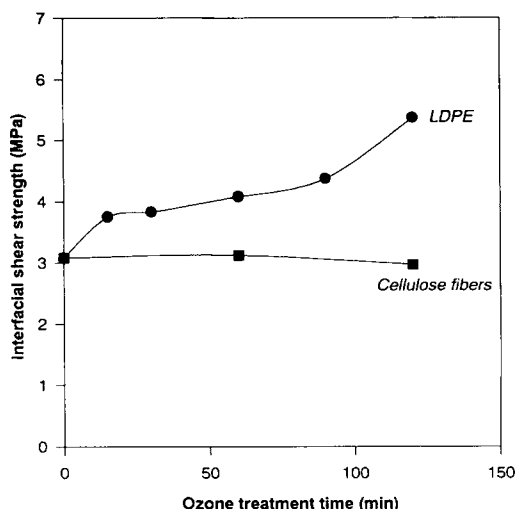


Figure 1 Interfacial shear strength (τ) as a function of ozone treatment time for LDPE film and regenerated cellulose fibers.

is significantly improved by the ozone treatment of LDPE, as can be seen in Figure 1. When LDPE is ozone treated for 120 min, the interfacial shear strength between cellulose fibers and LDPE increases from 3.1 MPa to 5.4 MPa, i.e., an improvement of 75%. In contrast, the ozone treatment of regenerated cellulose fibers was not successful in improving the interfacial adhesion. Even an extension of the ozone treatment time for cellulose fibers up to 480 min did not result in any noticeable improvement of the interfacial shear strength, as seen in Table I. Neither was the interfacial adhesion significantly affected by the ozone treatment of both LDPE and cellulose fibers, as compared with LDPE treated with ozone for equally as long a duration and untreated cellulose fibers (Table I).

With this background, and with the aim of clarifying the role of ozone in the improved interfacial adhesion observed for ozone-treated LDPE, an extensive surface characterization was performed.

Surface Characterization

The level of oxidation of the surfaces of the ozone-treated materials was determined by ESCA, and the analysis showed that oxidation took place on the materials, which is coherent with other reports concerning ozone treatment (Table II).¹⁵⁻²¹ No trace of oxygen was found on the original spectrum of LDPE, while a peak at 535 eV corresponding to oxygen species developed after 120 min of ozone treatment. Analysis of the area under the peaks shows that the oxygen to carbon (O/C) ratio increases from 0 to

Table I The Effect of Simultaneous Ozone Treatment of Regenerated Cellulose and LDPE on Interfacial Shear Strength (τ)

Treatment Time for Rayon Fibers (min)	LDPE Untreated (MPa)	LDPE Ozone Treated 30 min (MPa)	LDPE Ozone Treated 90 min (MPa)
0	3.1	3.8	4.4
60	3.1	3.9	4.6
120	3.0	4.3	4.6
240	3.5	4.2	4.6
360	3.1	—	—
480	2.6	—	—

0.02 after 120 min of ozone treatment. Similarly, the O/C ratio for regenerated cellulose membranes increases from 0.70 to 0.76 after 480 min of ozone treatment, which corresponds to a 2% change in oxygen concentration. The amounts of oxygen species formed on the regenerated cellulose membranes and the LDPE film are thus similar but, as the membranes were treated four times longer it can be concluded that LDPE is more susceptible than regenerated cellulose to surface oxidation by ozone. Resolution of the C_{1s} -peaks of untreated and ozonized materials did not point out any significant differences.

However, carbonylic compounds were detected with ATR-FTIR to be among the oxygen-containing compounds formed on the ozone-treated surfaces. The ATR-FTIR spectra for different durations of ozone treatment of LDPE and regenerated cellulose membranes are shown in Figures 2 and 3, respectively. Figure 4 displays the ratio between the characteristic carbonylic peak and the reference peak for each material relatively to the ratio of an untreated sample. The carbonylic peak develops more rapidly for ozone-treated LDPE as compared with the regenerated cellulose membranes. Although it is

Table II Atomic Oxygen to Carbon (O/C) Ratios of Ozonized Materials as Measured by ESCA

	% C	% O	O/C
LDPE			
Untreated	100	0	0
Ozone treated 120 min	97.9	2.1	0.02
Cellulose membrane			
Untreated	58.9	41.1	0.70
Ozone treated 480 min	56.9	43.1	0.76

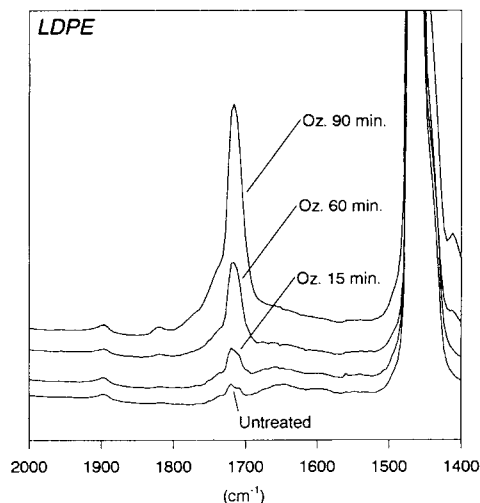


Figure 2 ATR-FTIR spectra on ozone-treated LDPE film.

not applicable to calculate the actual concentrations of carbonyls, it is proposed, in agreement with ESCA, that LDPE is more susceptible than regenerated cellulose to carbonyl formation by ozone treatment. Not surprisingly, the oxidation is mainly a surface phenomenon for both materials. The carbonylic peaks seen on the transmission spectra of the LDPE film and the cellulose fibers are far smaller for both materials as compared with the peaks on the surface spectra. For example, the relative carbonylic index for LDPE that has been ozone-treated for 120 min is about 10 times higher for the surface spectrum than for the transmission spectrum.

All new peaks that develop during the ozone treatment of LDPE are located in the carbonylic absorbance region at $1850\text{--}1700\text{ cm}^{-1}$. As seen again in Figure 2, many peaks are overlaid on each other, which renders difficulties in making an exact establishment of the chemical species responsible for the different peaks. However, the main peak at 1714 cm^{-1} corresponds to the position of ketones. The overlaid peak at 1740 cm^{-1} can be explained by crosslinking in the form of ester linkages, but may also hide peaks that can originate from free carboxylic acids. Another possible crosslink is made by anhydrides, which are observed from the small but noticeable peaks at 1775 and 1830 cm^{-1} .

Ketones and carboxylic acids are among the main species discussed in earlier studies, although the relative amount formed seems to vary considerably.¹⁵⁻²¹ Furthermore, the reports show that there are usually some differences for the development of other species represented by smaller peaks. The discrepancies between the different reports are understandable

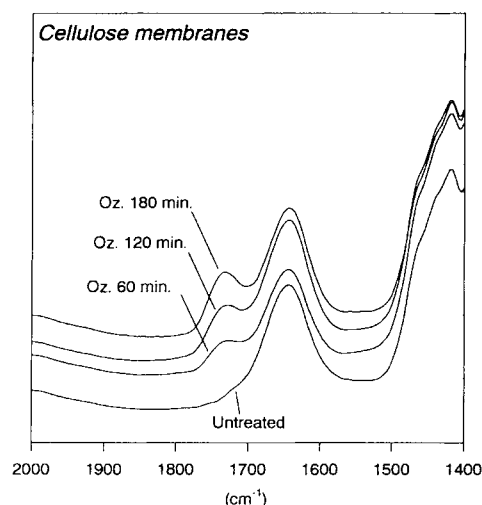


Figure 3 ATR-FTIR spectra on regenerated cellulose membranes.

considering the well-known complexity of oxidative procedures. For example, during the course of a thermo-oxidation process the species formed varied considerably.²² It is reasonable to assume that a similar variation occurs during ozone treatment as well. Hence, variation of important factors such as type and time of treatment, choice of material (stabilizers, chain branching, crystallinity etc.) will greatly affect the reaction scheme. Furthermore, the determination and interpretation of the oxidation products formed may be affected by the method of analysis.

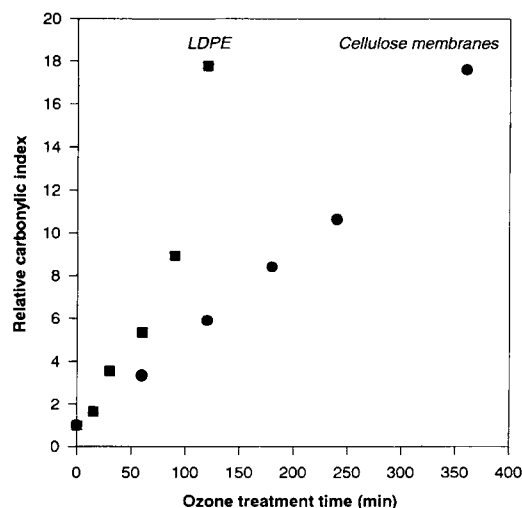


Figure 4 Carbonylic index of ozone-treated LDPE film and regenerated cellulose membranes as compared with untreated samples. The carbonylic indices for LDPE and cellulose are calculated from the absorbance ratios $1720\text{ cm}^{-1}/2020\text{ cm}^{-1}$ and $1735\text{ cm}^{-1}/1430\text{ cm}^{-1}$, respectively.

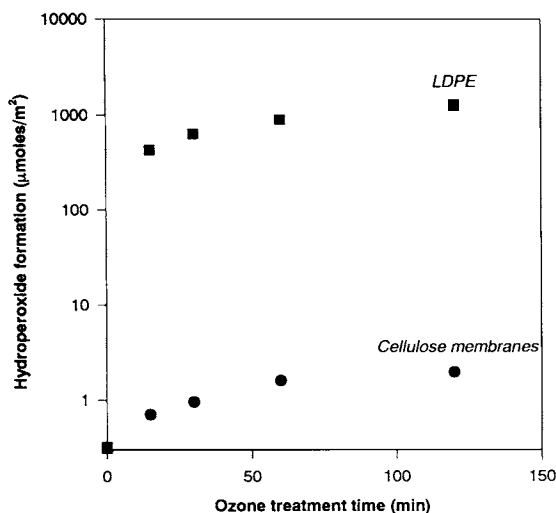


Figure 5 Hydroperoxide formation owing to ozone treatment, i.e., the concentration of hydroperoxides on ozone-treated surfaces in relation to untreated surfaces. Notice the logarithmic scale.

Despite all these factors producing dissimilarities in surface chemistry there are also reports that are in agreement. Hence the infrared spectra and the carbonylic index of ozone-treated polyethylene shown by Yamauchi and co-workers are almost identical to those reported here.²³

Moving on to the characterization of ozone-treated regenerated cellulose membranes, we found a broad peak at 1735 cm^{-1} , which is designated to different types of overlaid carbonyl groups (Fig. 4). In contrast to LDPE, it is not practically possible to resolve this peak in its components at all. No other significant changes are observed in the ATR-FTIR spectra and for that reason we avoid any speculations about the oxidation products on regenerated cellulose. The literature concerning the action

of ozone on the surface chemistry of cellulose has reported similar results.^{7,24}

Neither ESCA nor FTIR was able to detect hydroperoxides on ozone-treated surfaces, although it was shown earlier that hydroperoxides are formed on several different materials during ozone treatment.^{18,24-26} However, using the more sensitive iodide method, hydroperoxides were detected in all ozone-treated materials (Fig. 5). It is noted that the level of hydroperoxides formed increases with increasing level of treatment, which is in accordance with the earlier reports. Also, it is noted that LDPE is considerably more susceptible to hydroperoxide formation during the ozone treatment.

The average level of hydroperoxide concentration on cellulose fibers was also investigated, but the occurrence of fiber bundles made the exact determination of hydroperoxide concentration on the fibers difficult. For this reason, no results for fibers are shown in Figure 5, although all hydroperoxide concentrations determined are in the same range as plotted for the cellulose membranes. Thus the measurements still support the proposed higher susceptibility of LDPE to hydroperoxide formation, considering the significant difference in concentration.

Degradation of the Materials

The oxidation of polymeric surfaces is, as mentioned, a very complex procedure also capable of causing chain scission of the macromolecules.²⁷ Degradation of the chains was detected by SEC and DP measurements, showing how the molecular weight decreases with increasing ozone treatment time (Table III). In the case of the LDPE, the whole molecular weight distribution is shifted toward lower molecular weight as seen on the SEC curve presented in Figure 6. Consequently not only the surface but the whole

Table III Molecular Weight and Strength of Regenerated Cellulose Fibers after Ozone Treatment: Molecular Weight and Polydispersity Index for LDPE

Ozone Treatment (min)	Cellulose Fibers (DP)	Cellulose Fibers Stress at Break (MPa)	LDPE (M_n)	LDPE (M_w)	LDPE (M_w/M_n)
0	267	363	16.500	63.600	3.8
15	—	—	14.500	63.500	4.4
30	—	—	14.500	60.400	4.2
60	245	—	12.900	55.100	4.3
90	—	—	11.500	52.400	4.6
120	—	—	11.200	48.800	4.4
240	217	293	—	—	—
480	200	232	—	—	—

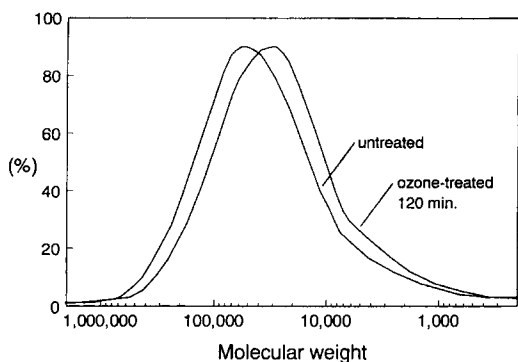


Figure 6 SEC curves of untreated and ozone-treated LDPE films.

bulk material of the film is degraded by the ozone treatment, which is interesting to note as the FTIR investigation showed that it is preferentially the surface that is oxidized during the treatment.

Furthermore, the filtration procedure prior to SEC analysis revealed no trace of crosslinking in terms of gel particles on ozone-treated LDPE. However, in agreement with the FTIR results showing that the major chemical changes take place at the surface, crosslinks may still be present in low concentration at the outermost surface layer.

For cellulose fibers, the decrease in molecular weight of the materials was associated with a subsequent decrease in tensile strength (Table III). For LDPE, neither the elongation at break nor the tensile strength was significantly affected. This is not surprising considering the nature of the highly oriented and anisotropic cellulose fibers as compared with the isotropic LDPE film.

There was no visual evidence of the degradation on either LDPE or regenerated cellulose fibers as seen by the SEM micrographs, which revealed no cracks or etching on the surfaces at 3000 times magnification.

Table V Surface Energies (γ) for LDPE and Regenerated Cellulose Fibers

	γ_{TOT} (mJ/m ²)	γ_D (mJ/m ²)	γ_P (mJ/m ²)
LDPE			
Untreated	29.3	28.8	0.4
Ozone treated	37.9	31.9	6.0
Cellulose fibers			
Untreated	67.0	33.0	34.0
Ozone treated	70.9	30.9	40.0

The ozone treatment time lasted for 120 min in both cases.

Adhesion Mechanism

The characterization of chemical and physical changes of ozone-treated materials provides a basis for the further explanation of the adhesion mechanism. In this sense, the newly formed groups' capability to form interactions and the nature of such interactions can be given by mapping the surface energies of the materials.

As expected, the ozone treatment affects the contact angles for different liquids with the surfaces and increases the total surface energies of both solids (Tables IV and V). More importantly, the oxidation procedure increases the polar component of the surface energy (γ^p) from 0.5 to 6.1 mJ/m² after 2 h of ozone treatment of LDPE. The increased polar character of LDPE will provide a significant better basis for interactions with the numerous hydroxyl groups on cellulose. More specifically, evaluation of the acid-base work of adhesion shows that the acid-base character of LDPE is significantly affected by the ozone treatment, whereas a minor change is observed for regenerated cellulose (Fig. 7). The great increase in the acid-base character of LDPE is seen for all three liquids used, i.e., formamide (Lewis base), ethylene glycol (Lewis acid), and water (bi-

Table IV Dynamic Contact Angles for Different Liquids with Regenerated Cellulose Fibers and LDPE Film

	Θ_{WATER} (deg)	$\Theta_{MET.IODIDE}$ (deg)	$\Theta_{FORMAMIDE}$ (deg)	$\Theta_{ET.GLYCOL}$ (deg)
LDPE				
Untreated	106.4 ± 2.6	62.5 ± 3.2	90.9 ± 1.41	80.0 ± 1.7
Ozone treated	88.8 ± 2.8	52.4 ± 1.7	70.0 ± 2.7	61.7 ± 4.2
Cellulose fibers				
Untreated	30.7 ± 5.9	25.4 ± 7.9	31.1 ± 11.3	22.5 ± 10.5
Ozone treated	19.9 ± 5.5	28.0 ± 6.3	26.4 ± 5.8	~0

The ozone treatment lasted for 120 min for both materials. Met. iodide: methylene iodide, Et. glycol: ethylene glycol.

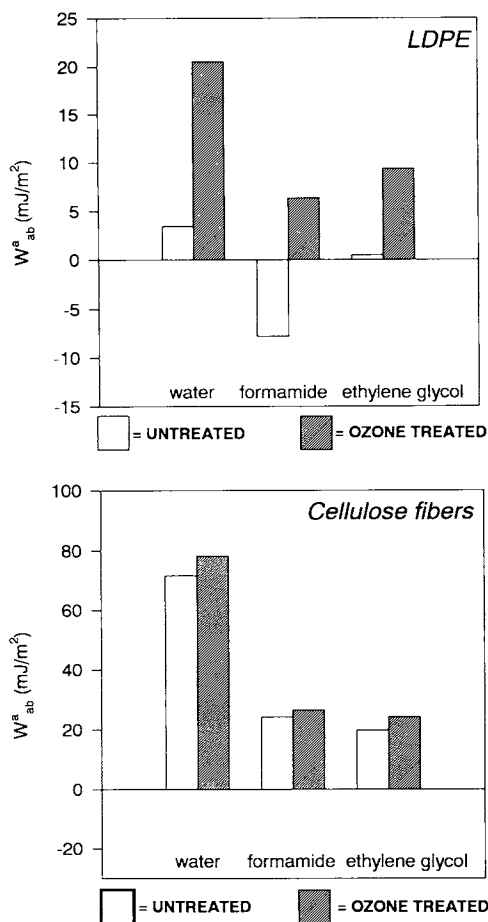


Figure 7 The acid-base work of adhesion for LDPE film and regenerated cellulose fibers as determined for different probe liquids.

functional), where a high work of adhesion parameter indicates an improved acid-base character. Hence, the improved ability of ozone-treated LDPE to form acid-base interactions will naturally enhance the matching of LDPE with cellulose, because cellulose has a naturally high acid-base work of adhesion parameter. The Lewis acid-base interactions include all types of sharing of electron pairs and thus hydrogen bonding is simply a specific case. However, on the basis of the chemical composition of cellulose and ozone-treated LDPE it is proposed that particularly hydrogen bonding plays a dominant role in the observed improved adhesion. The proposed mechanism is shown schematically in Figure 8 and involves hydroxyls on cellulose and carbonyls formed by ozone treatment on LDPE, as seen from the chemical characterization.

Regenerated cellulose also contains carbonyls in different forms but, in contrast to LDPE, enhanced interaction will not be gained by increasing the al-

ready high polar component of the surface energy or the acid-base work of adhesion parameter. In this context, oxidation of the already oxygen-rich cellulose surface will be of little if any advantage, since there is a very low native concentration of oxygen-containing groups on LDPE that have the ability to form strong interaction (imagine Fig. 8 with an untreated LDPE).

In this context, other possible adhesion mechanisms must not be forgotten. Hydroperoxides may decompose into alkoxy and hydroxyl radicals at temperatures above 150°C , or at lower temperatures when specific catalysis is performed.²⁷ Considering the high reactivity of radicals with most molecules, there are possibilities of crosslinking within the material as well as formation of covalent bonds between different materials, for example during processing (Fig. 9). The occurrence of covalent bonds between the two materials, even in low amounts, would inevitably improve the adhesion. The iodide method shows that a total press time of 2 min at 140°C decreases the concentration of hydroperoxides on the surface from $1270 \mu\text{mol/m}^2$ to $580 \mu\text{mol/m}^2$. Thus the hydroperoxides are decomposed during the lamination procedure, which means that there is a possibility of formation of interfacial covalent bonds between LDPE and cellulose.

A lamination experiment was performed to illuminate the role of hydroperoxides in the adhesion mechanism. Two LDPE films, one untreated and one ozone treated, were used to laminate two corresponding untreated regenerated cellulose films. An extraction of unbound LDPE material was then performed with the aim of revealing covalent bonding. The lamination procedure took place under the same circumstances as the manufacturing of samples for the SFF test, with the exception that the regen-

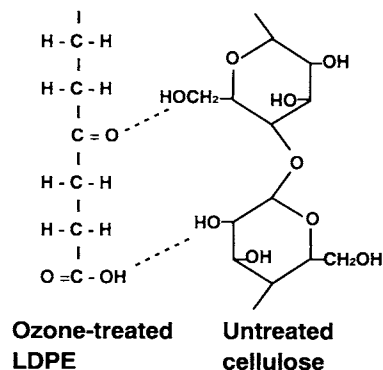


Figure 8 The proposed adhesion mechanism for ozone-treated polyethylene and cellulose on the basis of hydrogen bonding.

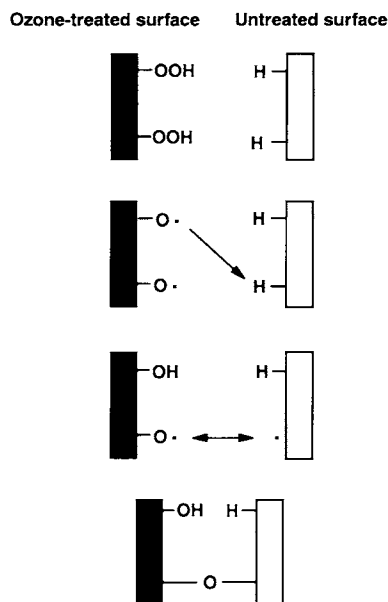


Figure 9 The proposed adhesion mechanism for an ozone-treated material with another surface on the basis of decomposition of hydroperoxides and covalent bonding.

erated cellulose was in the form of a smooth-surface film (cellophane) instead of a porous membrane in order to facilitate the extraction by *p*-xylene. The ESCA result shows how the surface chemical composition (O/C) of the cellophane laminated with untreated LDPE after the extraction step is comparable with pure cellophane (Table VI). In this case, it was possible to remove all LDPE during the extraction step. However, when the LDPE is ozone-treated prior to the lamination, the O/C-ratio decreases considerably as compared with the pure cellophane sample. This indicates the presence of LDPE on the cellulose surface. It is thus evident that this is the result of strong interactions between the cellulose and LDPE, which prevent the removal of a thin layer of LDPE during the extraction. However, it is still indirect proof of the presence of covalent bonds between the surfaces as other strong forces, such as hydrogen bonding, may also prevent solvation to some degree.

Considering that ozone treatment of cellulose also leads to the formation of hydroperoxides, but no improvement of adhesion as seen from the SFF test, it may seem unlikely that covalent bonding alone could promote the interfacial adhesion. However, one should be cautious in drawing the conclusion that hydroperoxides are not active in improving adhesion in either case. Mainly, as discussed earlier in connection to Figure 5, the concentration of hydroperoxides on the cellulose fibers is radically lower

than that on LDPE. This must be of great importance if hydroperoxides are active in enhancing adhesion. Another thing worth considering is the question of the probable reactions of the cellulose molecules as compared with the LDPE molecules. A possible reaction for the "LDPE-based" radical across the interface is the abstraction of a hydroxylic group in the cellulose chain. The corresponding reaction for the radical produced on the cellulosic molecule would be the abstraction of a hydrogen directly from the LDPE hydrocarbon chain. Differences in energy barrier and rate for these reactions must be taken into account in order to determine whether both types of radical have an equal ability to form interfacial covalent bonds.

One may also argue that crosslinking and etching resulting from the ozone treatment are often important to the interfacial adhesion. Physical changes causing stiff interfaces (crosslinking) and topographically rougher surfaces may improve the adhesion by mechanical interlocking. Another important factor that can affect the adhesion characteristics is the removal of impurities on the surface that take place during etching. However, we suggest on the basis of SEM and SEC investigations that the physical changes are not significant enough to be of any importance to adhesion in this case.

To summarize, we propose that the mechanism responsible for the improved adhesion between cellulose and LDPE noted when LDPE is ozone-treated is a result of two indistinguishable effects, hydrogen bonding between oxidation products on LDPE and cellulosic hydroxyls, and covalent bonding originating from the decomposition of hydroperoxides.

In 1969, Goring and Suranyi made a study that at first glance might seem to contradict the results presented here.⁷ They found that the bond strength of laminates was increased considerably by ozone treatment of both deacetylated cellulose and polyethylene as compared with treating polyethylene alone. However, in this case, a mixture of ozone and ammonia was used, which was observed to be more effective than ozone itself. The special procedure results in a surface chemistry different from that

Table VI Atomic Oxygen to Carbon (O/C) Ratios on Extracted LDPE/Cellophane Laminates

	% O	% C	O/C
Cellophane	35.5	64.5	0.55
Cellophane laminated with LDPE	35.1	64.9	0.54
Cellophane laminated with ozone treated LDPE	8.6	91.3	0.10

produced by pure ozone, and the authors also observed that the ammonia/ozone treatment neutralizes the carboxylic groups and causes etching of the surface. The differences in surface chemistry may alter the reaction scheme radically and may thus also affect the adhesion characteristics. The increased etching is also worth noting as important to adhesion in the sense of mechanical interlocking and cleaning of surfaces.

CONCLUSIONS

The interfacial adhesion between regenerated cellulose fibers and low-density polyethylene is increased by treating LDPE with ozone. Both LDPE and regenerated cellulose are oxidized during the ozone treatment, which results in the formation of carbonyl and hydroperoxide. The carbonyls on LDPE are mainly ketones and carboxyls. The improved adhesion is proposed to occur on the basis of both hydrogen and covalent bonding. Carbonyls on LDPE can interact with hydroxyl groups on cellulose, and hydroperoxides may decompose during processing to form strong bonds between the materials. Chain scission takes place for both materials when exposed to ozone, but the physical and mechanical changes are limited as long as the treatment is not extended.

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