10-2.- Structural Characterization of different Composites

EFFECTS OF DIFFERENT TREATMENTS ON THE INTERFACE OF HDPE / LIGNOCELLULOSIC FIBER COMPOSITES

composites science and technology

Prof. Xavier Colom

aim

We studied the chemical and mechanical characteristics of composites made up of HDPE and lignocellulosic fibers (in the presence or absence of a coupling agent). Interfacial morphology and esterification reactions between aspen fibers and the coupling agent were analyzed by means of FTIR and SEM. The variation of absorption in spectral bands was determined in order to assess the influence of the coupling agents as well as the lignocellulosic fiber content. SEM micrographs were used in order to show the “bridge effect”, brought about by the coupling agent between the HDPE matrix and the reinforcement of lignocellulosic fibers. Mechanical properties, such as TS, EM, elongation at breaking point and toughness, were also analyzed. Finally, the differences observed between the various composites studied were explained by some specific adhesion mechanisms.

experimental part

materials used

HDPE 2909 of Du Pont Canada,

fluidity index=1.35g/min and density 0.96 g/cm3.

Cellulosic fibres were short fibres of aspen (populus tremula), whose length/diameter ratio is L/D=8,7.

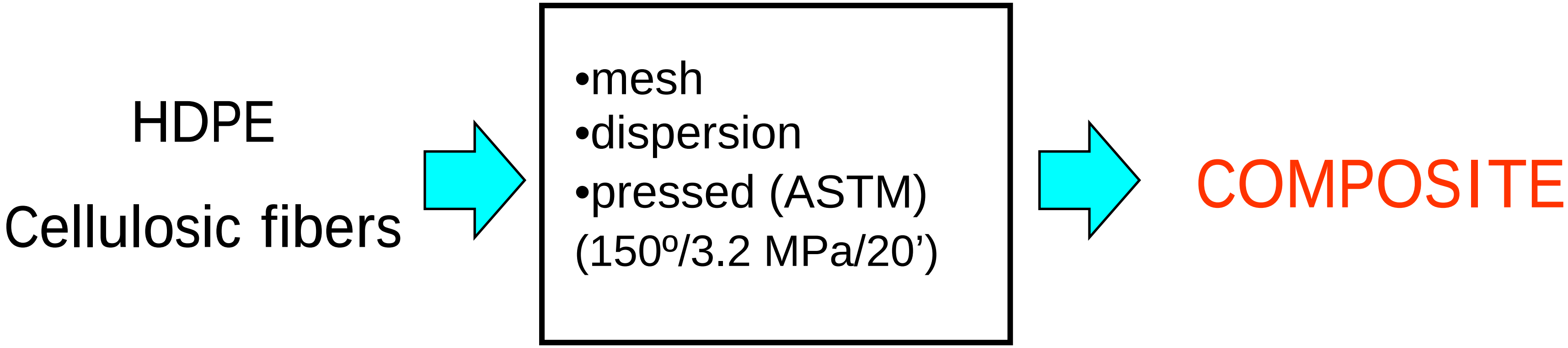
Silane A-174 of Union Carbide used as a coupling agent to improve the hydrolytic stability of the matrix reinforcement interface

Epolene C-18 supplied by Eastman Chemical Products Inc.

experimental part

how to make this composites

without coupling agents



HDPE

Cellulosic fibers

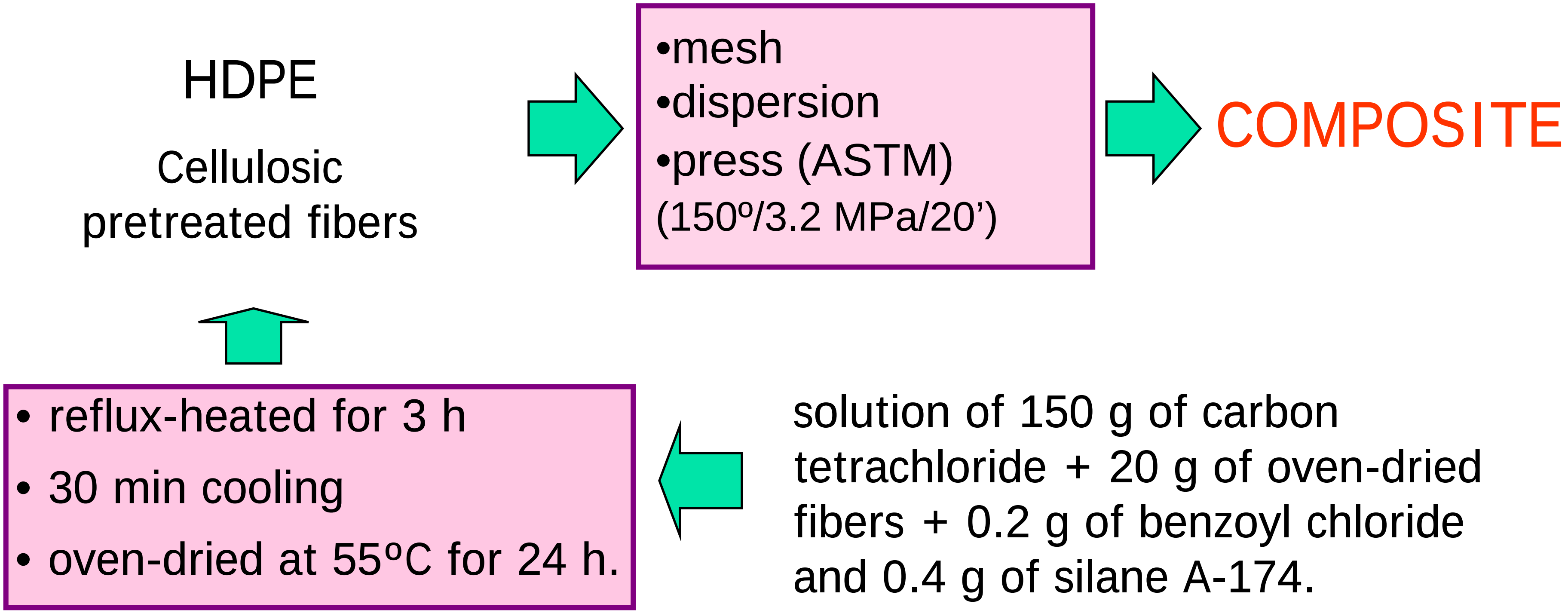
- mesh
- dispersion
- pressed (ASTM) (150º/3.2 MPa/20’)

COMPOSITE

experimental part

how to make this composites

with silane coupling agents



HDPE

Cellulosic pretreated fibers

- mesh
- dispersion
- press (ASTM)

(150º/3.2 MPa/20')

COMPOSITE

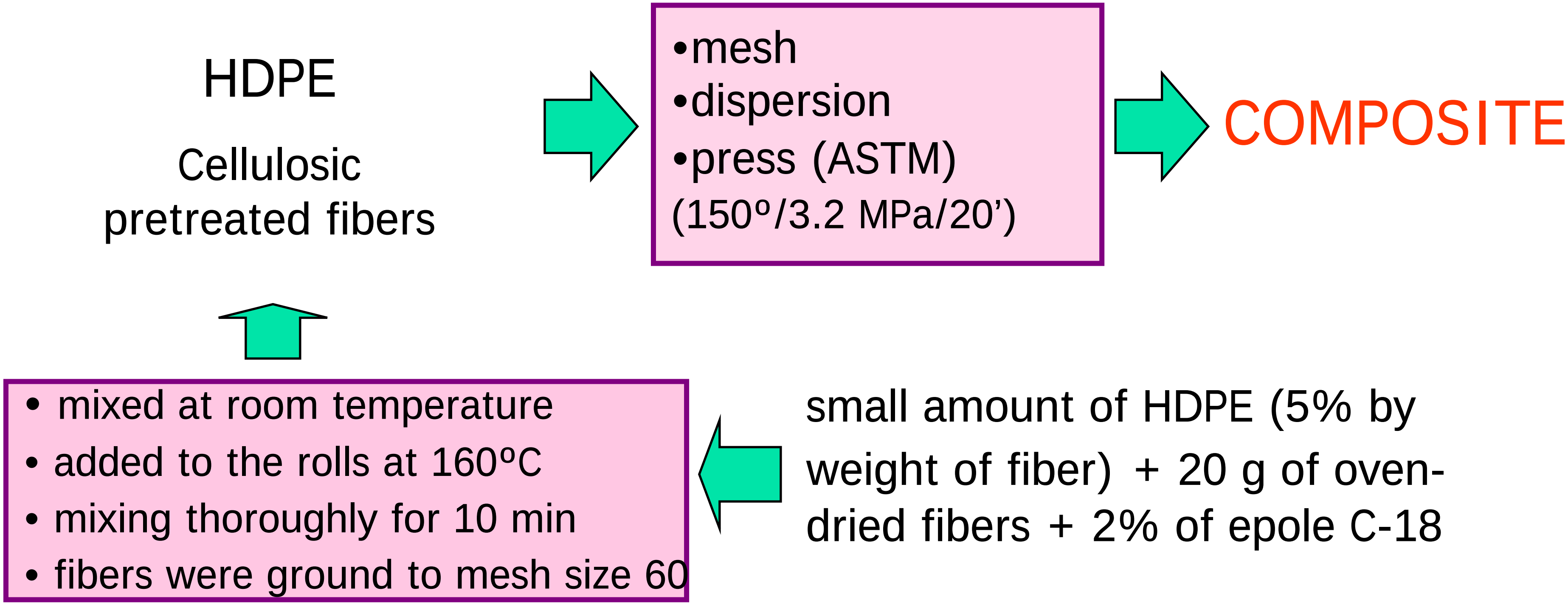
- reflux-heated for 3 h
- 30 min cooling
- oven-dried at 55ºC for 24 h.

solution of 150 g of carbon tetrachloride + 20 g of oven-dried fibers + 0.2 g of benzoyl chloride and 0.4 g of silane A-174.

experimental part

how to make this composites

with epolene coupling agent



HDPE

Cellulosic pretreated fibers

- mesh
- dispersion
- press (ASTM)

(150º/3.2 MPa/20’)

COMPOSITE

- mixed at room temperature
- added to the rolls at 160ºC
- mixing thoroughly for 10 min
- fibers were ground to mesh size 60

small amount of HDPE (5% by weight of fiber) + 20 g of oven-dried fibers + 2% of epole C-18

experimental part

Spectrophotometry FTIR

FTIR spectra were obtained by means of a Nicolet 510 M spectrometer with CsI optics. Samples of the material surface, 9 mg finely divided, were ground and dispersed in a matrix of KBr (300 mg), followed by compression at 167 MPa to consolidate the formation of the pellet. Reduced absorbance values were used in order to avoid the spectral differences arising from the preparation of KBr pellets.

experimental part

mechanical testing

- In each series, a minimum of six samples were tested according to ASTM D-638 procedure. The full-scale load was 5 KN and the cross-head speed was 10 mm/min. The test results were automatically calculated by a HP 86B computing system using Instrom 2412005 General Tensile Test Program.

- Izod-impact tests (unnotched) were performed in a TMI 43-01 Impact Tester. The coefficient of variation of the reported properties was less than 6%.

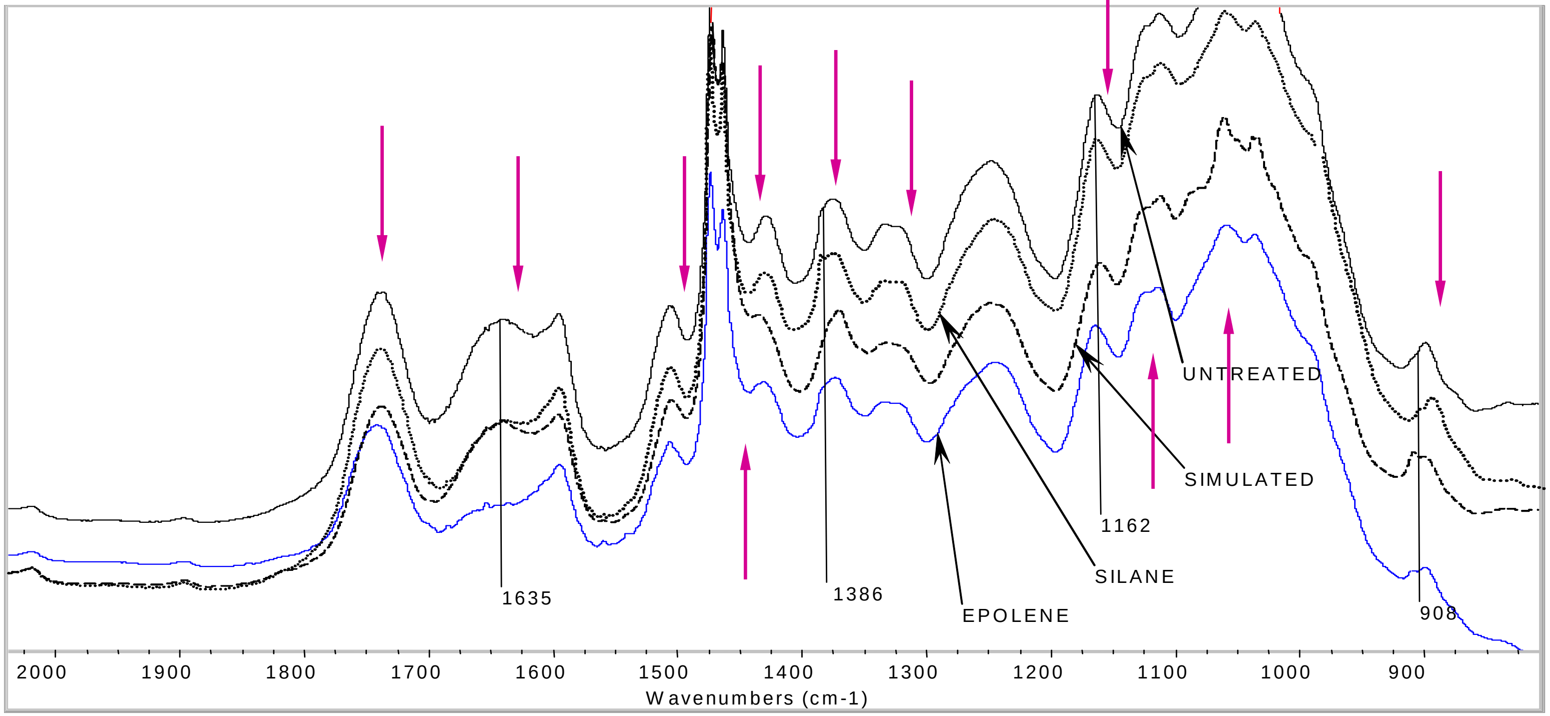
experimental part

Scanning electron microscopy

(SEM) was used to examine qualitatively the dispersion and adhesion at the interface between lignocellulosic fibers and polyethylene matrix. The surface o molded composites was examined with a Zeiss DSM 960 scanning electron microscope. Dry samples were coated with a thin layer of carbon before observation under the microscope, in order to increase the sample conductivity.

results

Wavenumber (cm^{-1})	***Assignment***
1740	C=O stretching of acetyl or carboxylic acid
1653/1635	Absorbed H_2O
1507	Aromatic bending C-H (ring)
1465	Lignin and CH_2 sym. bending pyran ring
1426	CH_2 bending (Cell)
1331	OH in plane bending (Cell)
1162	Antisym. bridge C-OR-C stretching (Cell)
1110	Anhydroglucose ring
1055	Stretching C-OR (Cell)
898	Antisym., out of phase ring stretching



results and discussion

FTIR spectra of composites with different coupling agents

- Figure shows the characteristic spectra of composites containing 40% of lignocellulosic fibers. It shows the bands involved in the interfacial interaction between the lignocellulosic reinforcement and the HDPE matrix, in the presence or absence of different types of coupling agents.

- Simulated spectra were obtained by means of the weighted spectral addition of each component of the composite. Comparing the composites spectra with the simulated ones, differences in the shape and intensity of the bands can be observed.

- The spectral band at 1386 cm-1 is due to structural changes, mainly conformational, generated by the interaction of the two components. The spectral band at 1635 cm-1 corresponds to water absorption, due to the hydrophilic character of the lignocellulosic fiber.

results

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1740	C=O stretching of acetyl or carboxylic acid
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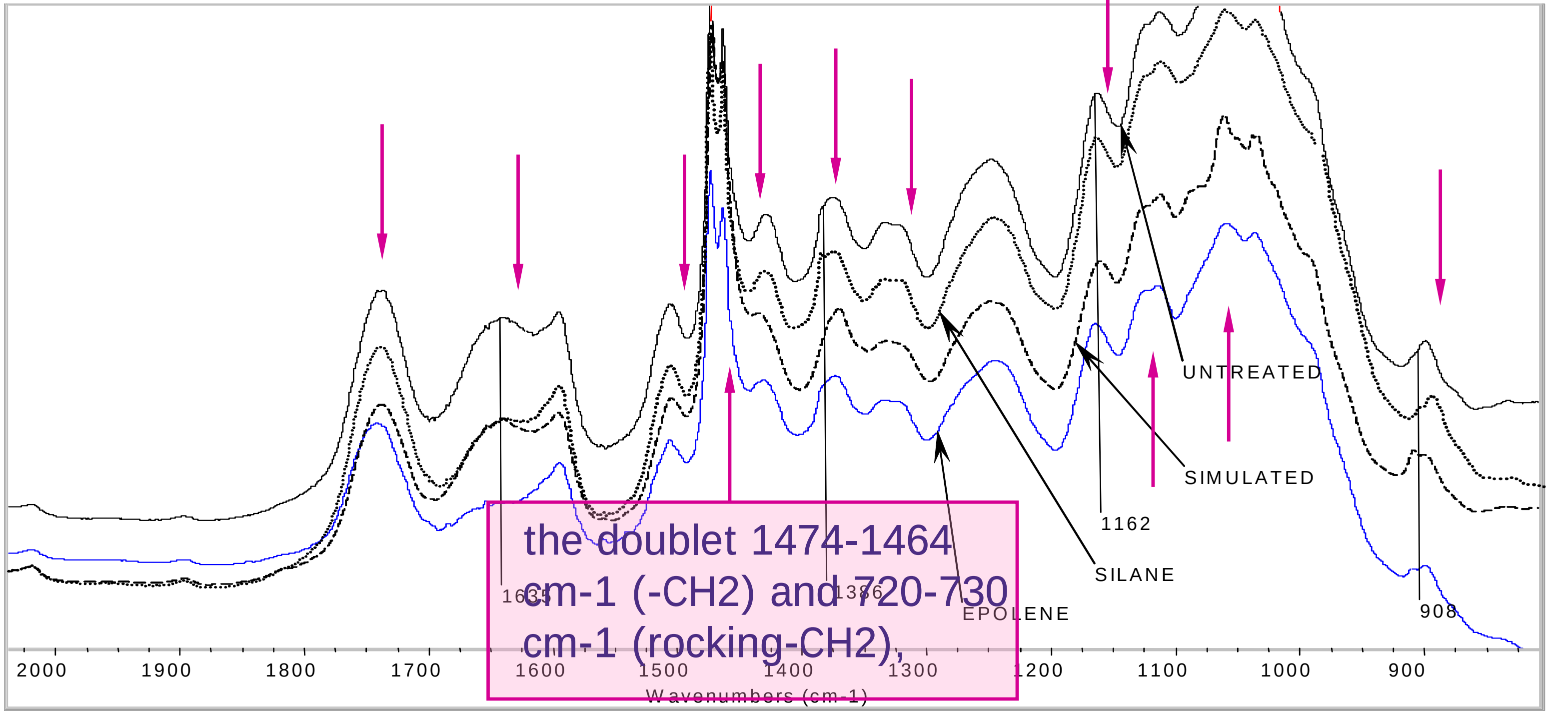

the doublet 1474-1464 cm-1 (-CH2) and 720-730 cm-1 (rocking-CH2),

results

Wavenumber (cm^{-1})	***Assignment***
1740	C=O stretching of acetyl or carboxylic acid
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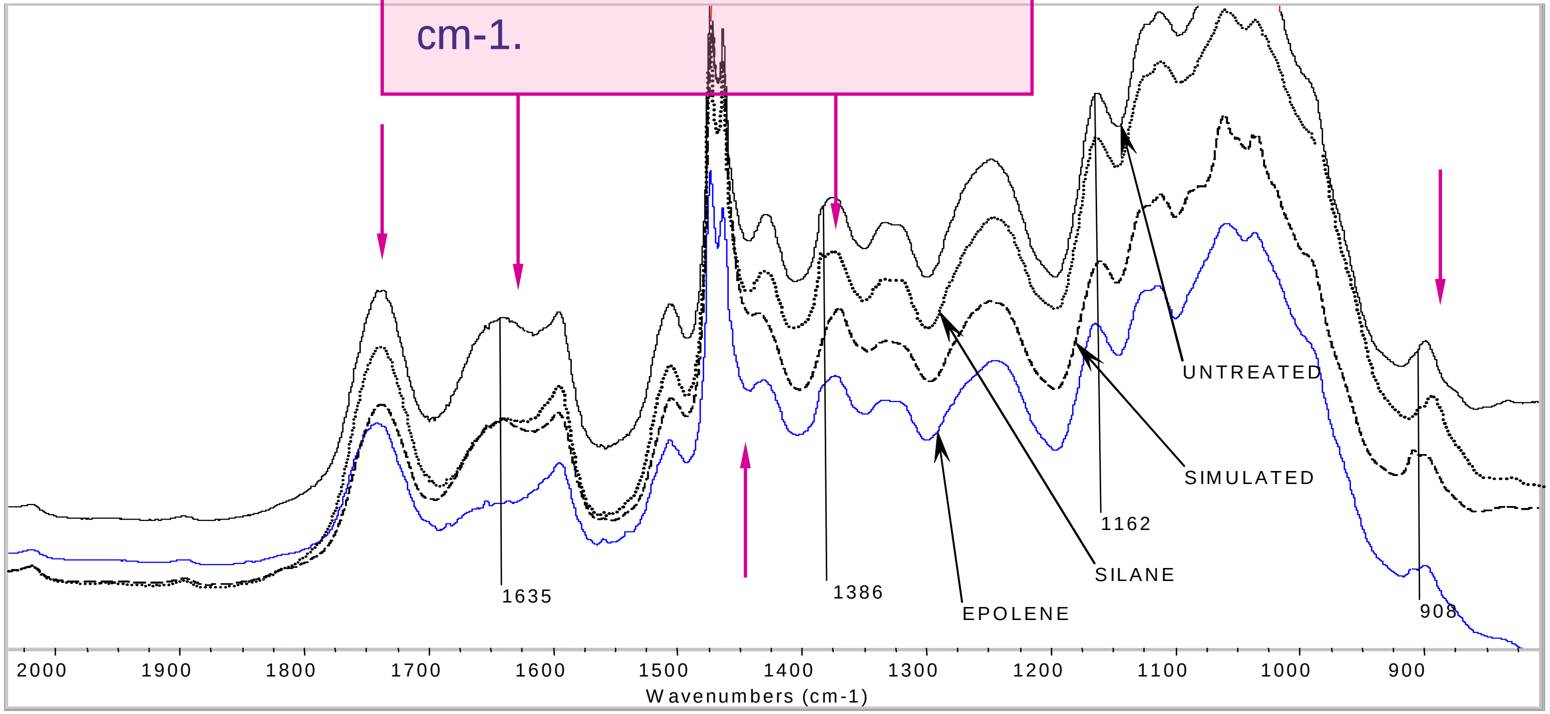
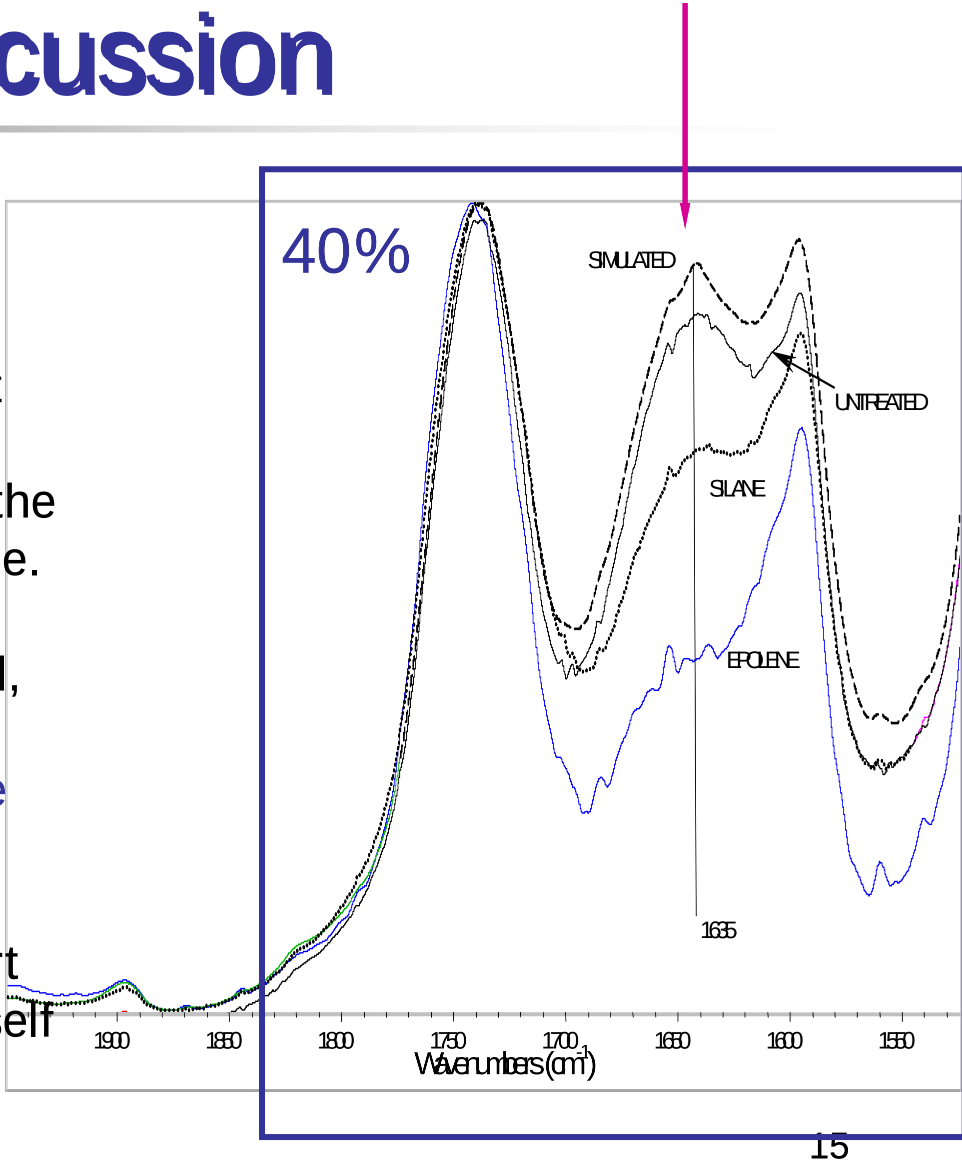
two special bands, belonging neither to the lignocellulosic fibers nor to the HDPE, are observed: 1386 cm-1 and 1635 cm-1.



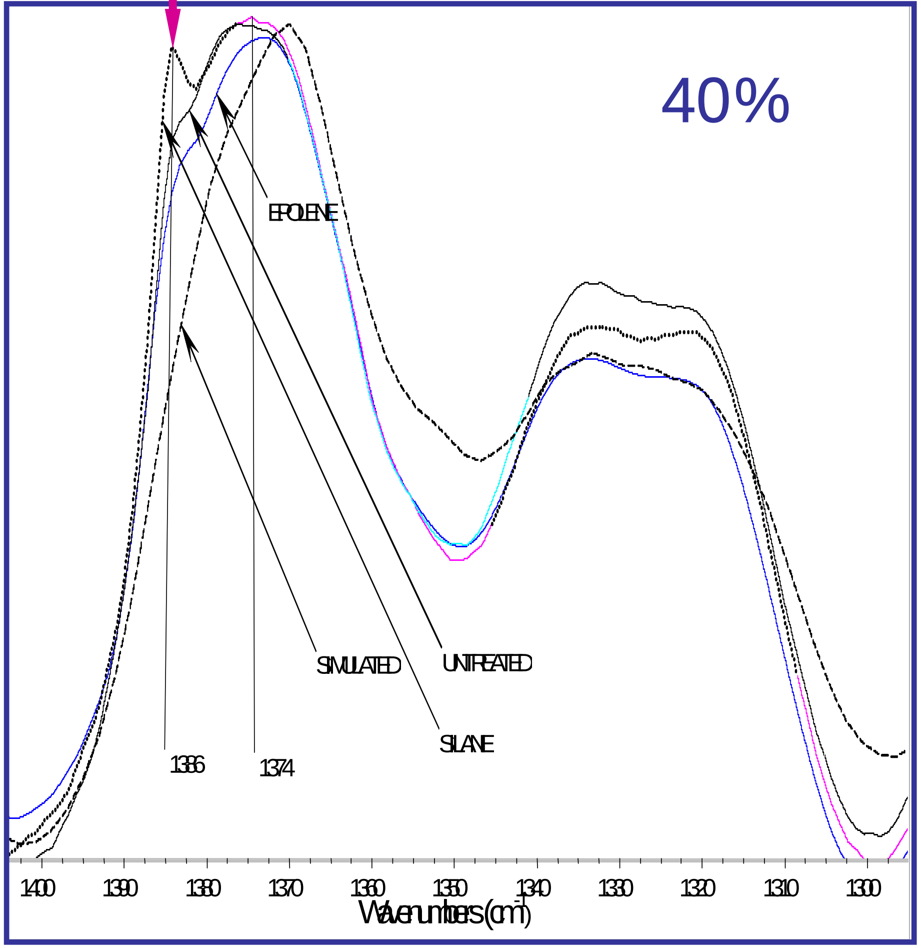
results and discussion

This fig shows the 1635 cm-1 band for different types of composites containing 40% of lignocellulosic fibers. The highest absorbance value corresponds to the untreated composites and the lowest to the ones modified with maleated polyethylene. The different patterns of this band, in relation to the types of treatment applied, is due to (i) the hydrophilic nature of the lignocellulosic fiber and (ii) the protective effect produced by the coupling agents (maleated polyethylene and silane). The maleated polyethylene probably uses part of the humidity absorbed to hydrolyze itself and to react with the fiber.



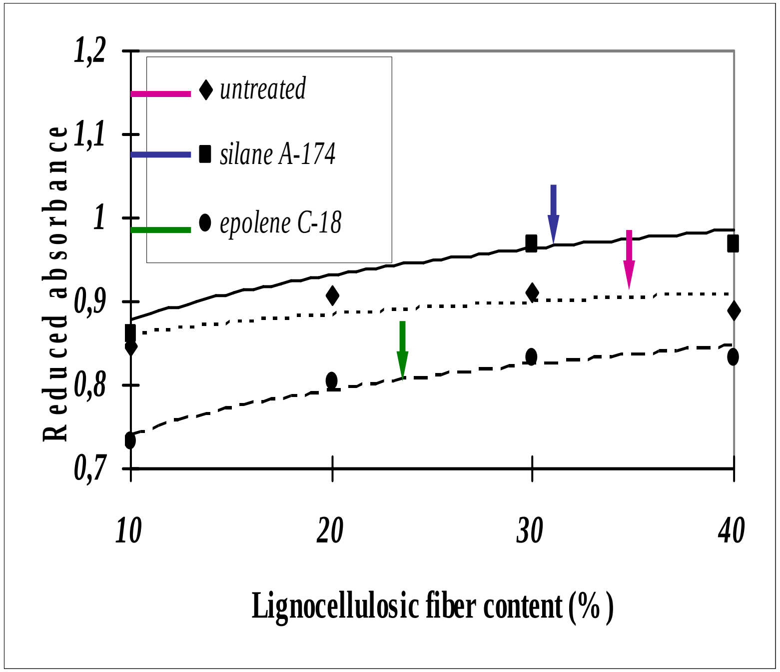
results and discussion

Fig shows the 1386 cm-1 band - associated with vibrational perturbations of glycosidic bonding in the cellulose backbone Spectra illustrates that the absorption varies in relation to the type of treatment. On the other hand, it has been demonstrated that the lignocellulosic fiber content is another variable to be taken into consideration, as shown in next graphic



results and discussion

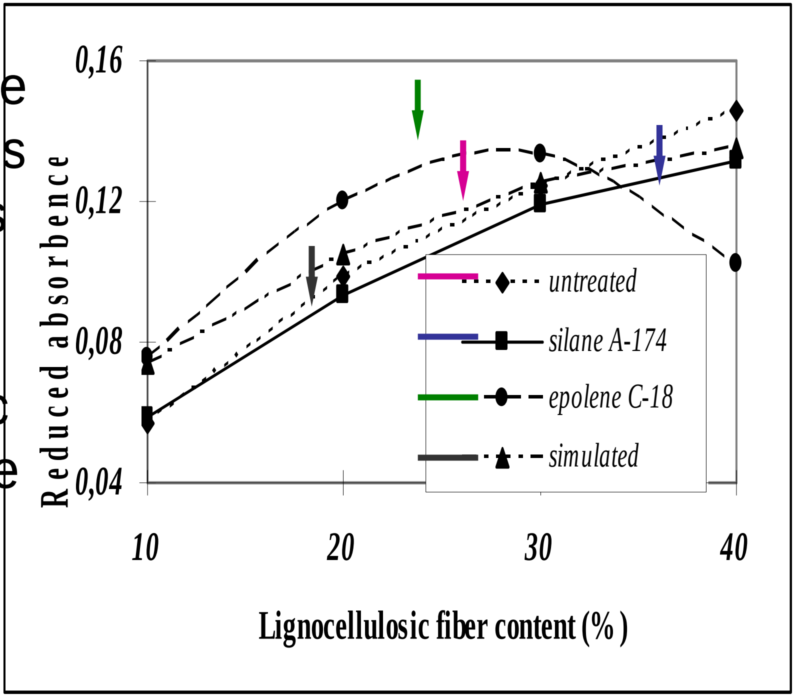
The highest value for reduced absorbance corresponds to the silane treatment and the lowest absorbance to the epolene treatment. The chemical structure of the silane molecule causes distortion, resulting in conformational changes, in the glycosidic bond. This is due to the electrostatic repulsion of the carbonyl and the terminal vinyl and to the steric interactions of the trimethoxysilane group. The maleated polyethylene is a surface modifier, less voluminous than silane, and thus its interaction with the glycosidic bond of the cellulose is weaker. Therefore the perturbation effect is less effective



1332 cm-1 band

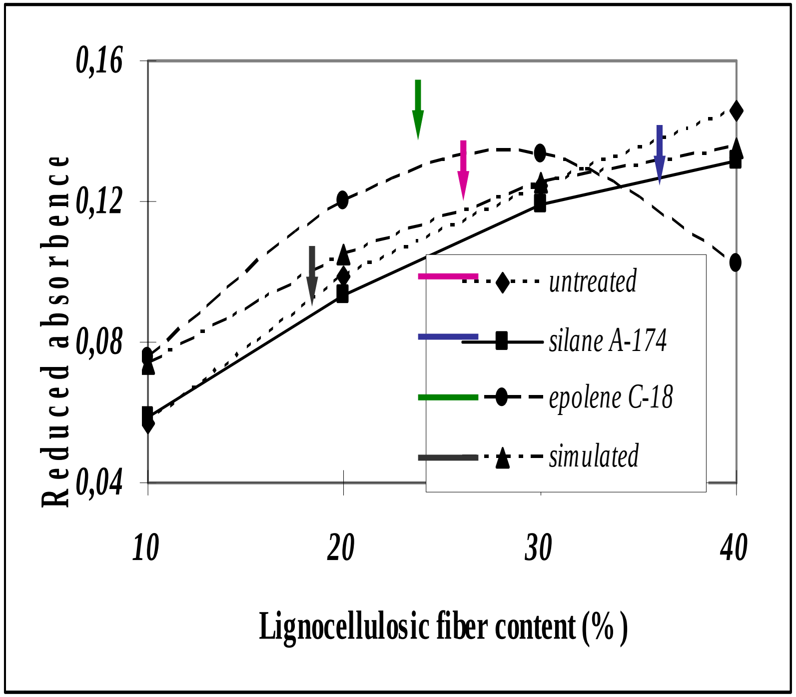
results and discussion

assigned to the bending of -OH groups in the cellulose component, depends on the percentage of lignocellulosic fibers and the type of treatment used. The evolution of this band is quite similar in all cases, except in the samples modified with maleated polyethylene. As expected, the content of hydroxyl groups increases with the percentage of lignocellulosic fibers. The lowest curve of reduced absorbance corresponds to silane treated composite. This can be explained as follows: Some of the hydroxyl groups of cellulose and the hydroxyl groups of silanol (obtained after hydrolysis of silane) react, thus generating an ether bridge.



results and discussion

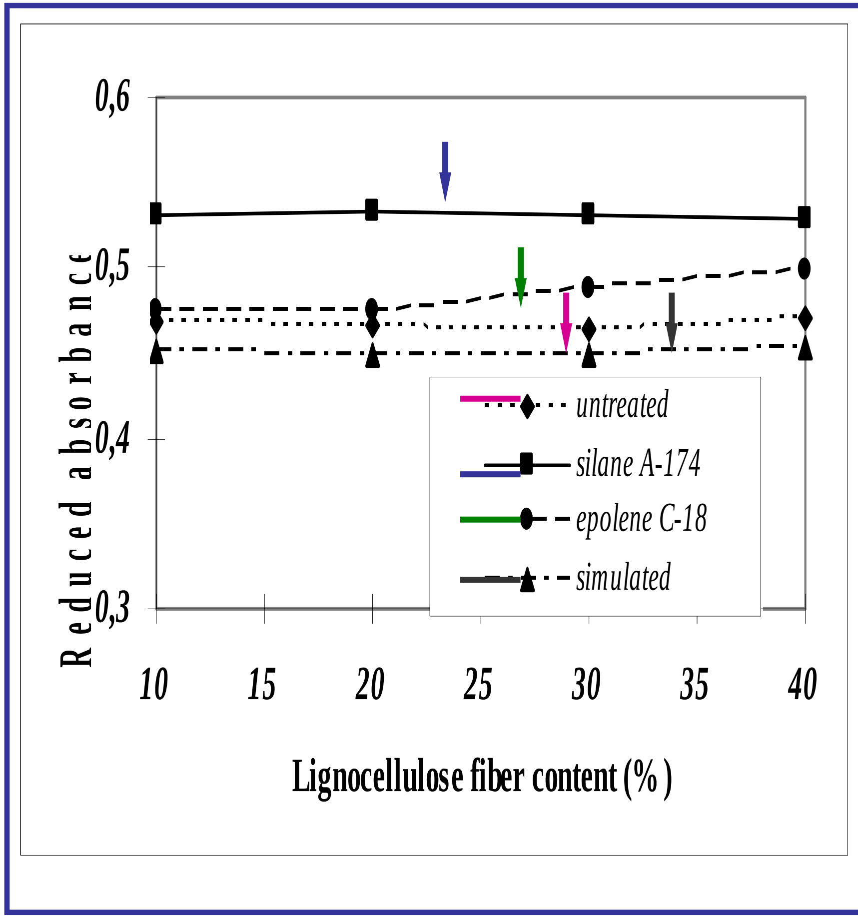
In contrast, the curve for reduced absorbance for untreated composites develops in parallel with that of simulated composites. However, the reduced absorbance of the composite modified with maleated polyethylene increases steadily as lignocellulosic fiber content rises to 30%, with a significant decrease afterwards. This behavior is due to the formation of hydroxyl groups coming from the hydrolysis of anhydride groups in maleated polyethylene with a subsequent transformation of these groups into an ether bridge.



results and discussion

It shows mainly the formation of an ether bond in the composites treated with silane and also, to a lesser extent, those treated with maleated polyethylene. The silane treatment leads to the highest value of reduced absorbance (i.e. highest content of ether bridges), which reveals the formation of a covalent bond between the silane and the lignocellulosic fibers. Composites treated with maleated polyethylene show a smaller value of reduced absorbance than composites treated with silane.

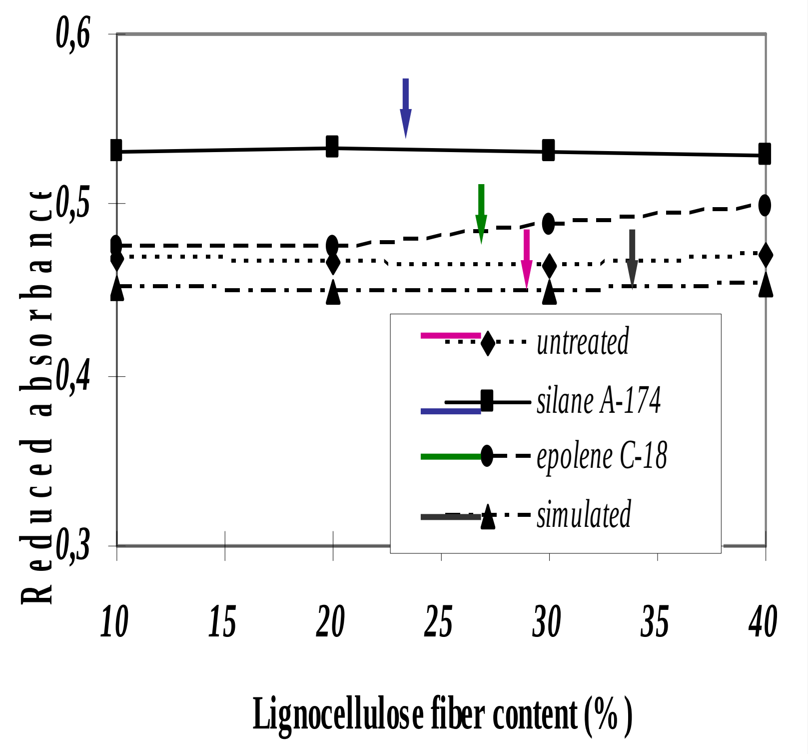
1162 cm-1 band
C-O-C stretching



results and discussion

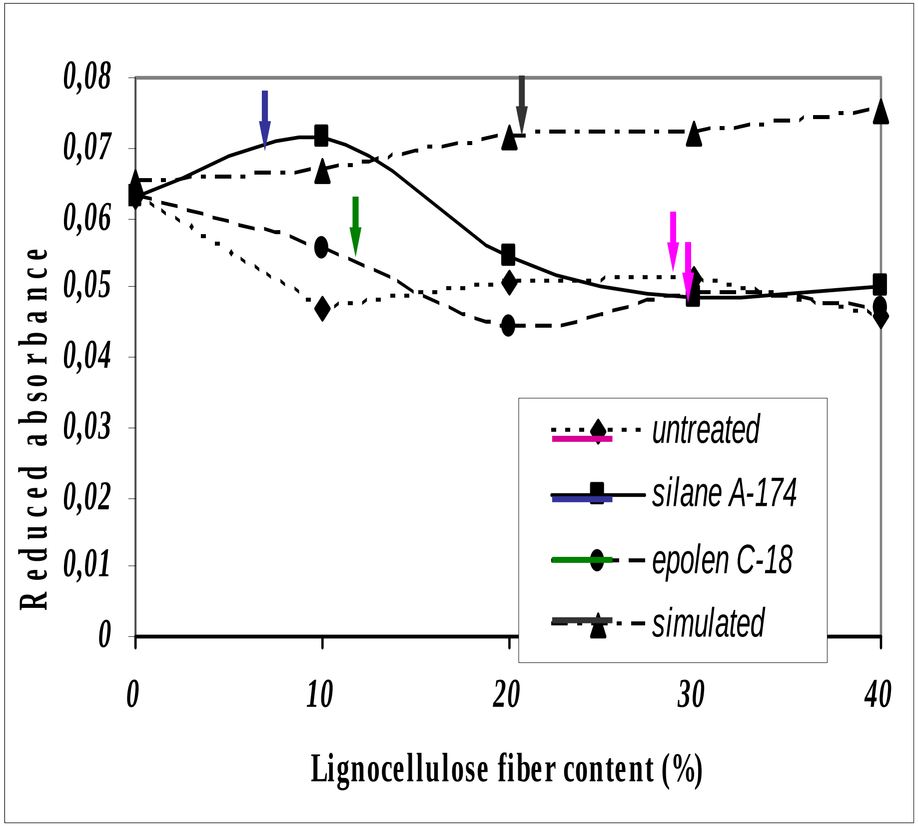
This behavior can be explained by taking into consideration the two following points

- the epolene treatment was not carried out by impregnation of the lignocellulosic fibers, as was the treatment with silane.
- In order to hydrolyze the maleated polyethylene, it is necessary to transfer water from the fiber to the matrix. When the percentage of fiber increases (i.e. the water content increases), then the number of hydroxyl groups increases, thus leading to a higher number of ether bridge formations.



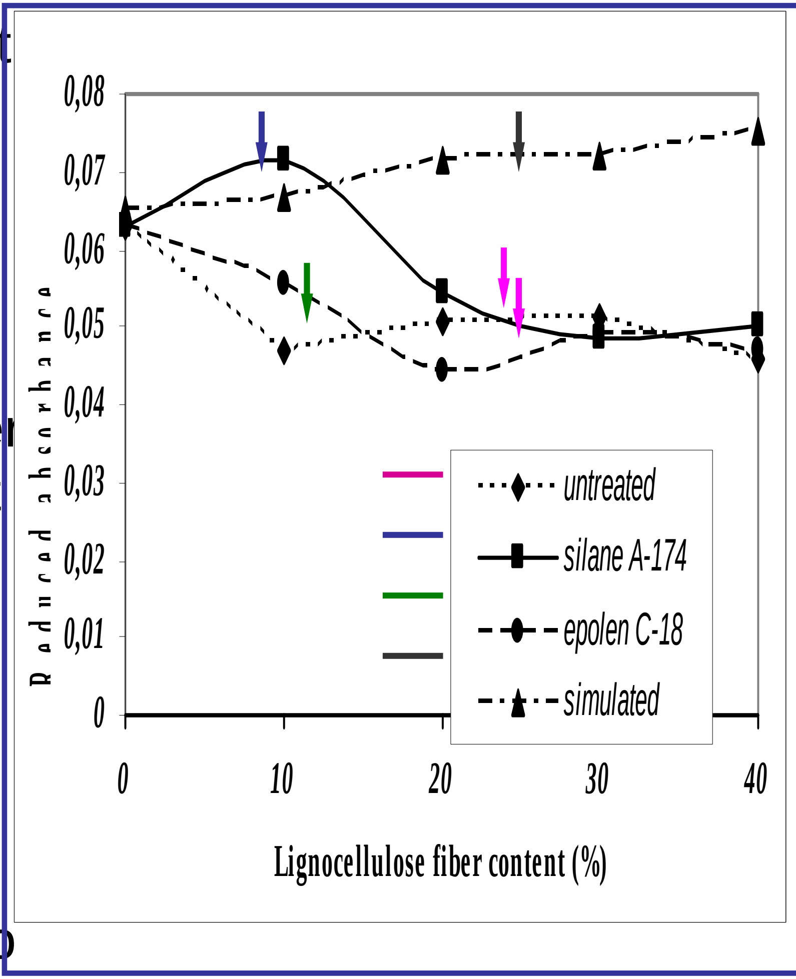
results and discussion

Figure shows the evolution of the reduced absorbance corresponding to the bending of the vinyl group (-CH=CH2, 910 cm-1). The reduced absorbance of composites treated with silane varies in a more complex way as lignocellulosic fiber content increases: From 0 to 10% of lignocellulosic fiber content there is an increase in reduced absorbance, then a decrease between 10 and 30% and finally it takes an asymptotic value at higher percentages.



results and discussion

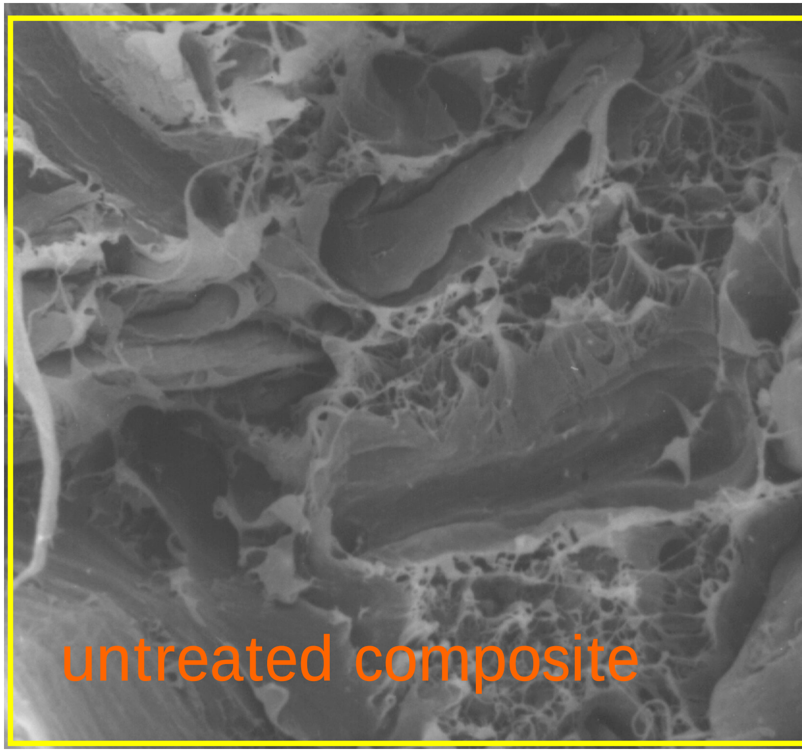
This behavior can be explained as follows: At low percentages of lignocellulosic fibers, the high proportion of HDPE obstructs the reaction capacity of the double bond in the silane. Therefore, the double bond content increases as the silane content increases (it must be noted that as the lignocellulosic fiber content rises, so does the silane content). At a fiber content of between 10 and 30%, the reaction capacity between the HDPE double bonds and those of the coupling agent increases, thus leading to a decrease in the vinyl group content. At higher lignocellulosic fiber content (more than 30%), all the reactive groups have reacted, thus leading to a constant vinyl group content.



results and discussion

SEM characterization of interfacial adhesion

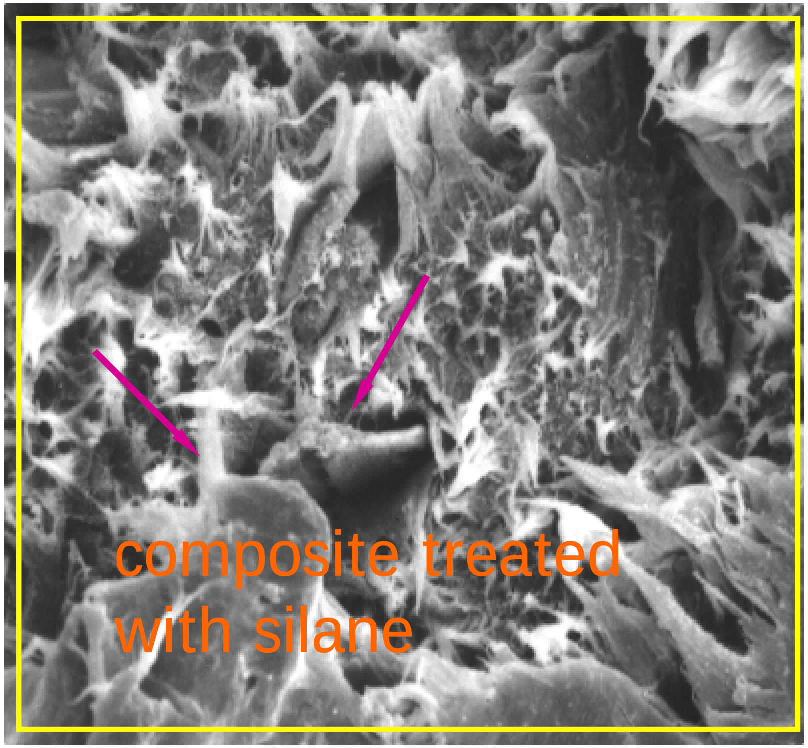
SEM micrographs of fracture surfaces of different composites (all containing 40% of lignocellulosic fibers) clearly indicate that the differences in microstructure of the various composites are significant, as shown in all Figures. In figure the untreated fibers appear to be free of any matrix material adhering to them. This is a clear indication of the poor adhesion between lignocellulosic fibers and HDPE



results and discussion

First of all, the addition of coupling agents enhances their dispersion in the continuous HDPE phase. More interestingly, the SEM micrograph also shows that the silane coupling agent facilitates the direct contact between the lignocellulosic fibers and HDPE matrix to a higher degree than in the untreated and epolene treated composites

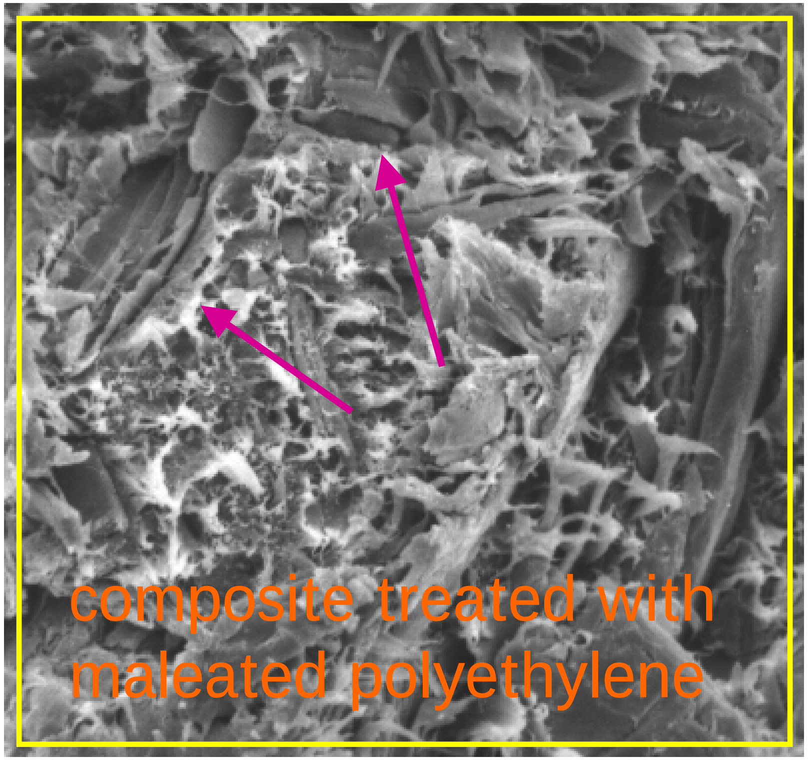
Figure shows the fracture surface for the composite with silane treated fibers. Fibers are still coated with HDPE and it can be seen that the matrix fractured by shear yield flow and tearing from the fiber



results and discussion

In the case of lignocellulosic fibers treated with maleated polyethylene, the fiber-matrix adhesion seems to be better. Although there is fiber pullout, some of them are coated with the HDPE matrix. It can also be observed that the break of the composites takes place by shear yield and tearing.

The differences between the failure surface of differently treated composites are attributed to the different chemical natures of the coupling agents and different adhesion mechanisms.



composite treated with maleated polyethylene

Lignocellulosic fiber content (%)	Tensile strength (MPa)	Young modulus (MPa)	Elongation at breaking point (%)	Toughness (J)
HDPE / Lignocellulosic fiber composites without coupling agent				
0	28.3	1470	23.2	0.132
10	27.5	2190	2.8	0.058
20	24.5	2410	2.65	0.055
30	20.8	2590	1.9	0.025
40	21.0	3070	1.6	0.022
HDPE / Lignocellulosic fiber composites treated with epolene				
0	28.3	1470	23.2	0.132
10	26.7	1804	5.3	0.085
20	24.5	2330	3.5	0.035
30	23.7	2750	2.3	0.025
40	24.5	3230	1.5	0.022
HDPE / Lignocellulosic fiber composites treated with silane				
0	28.3	1470	23.2	0.132
10	30.2	1820	6.2	0.123
20	33.1	2330	5.7	0.067
30	37.9	2614	5.4	0.111
40	44.5	3190	4.1	0.085

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40				0.022
0				0.132
10				0.085
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30				0.025
40				0.022
0	28.3	1470	23.2	0.132
10	30.2	1820	6.2	0.123
20	33.1	2330	5.7	0.067
30	37.9	2614	5.4	0.111
40	44.5	3190	4.1	0.085

Table shows the variation of various mechanical properties as a function of the nature of the coupling agent used and the lignocellulosic fiber content in composites. The importance of the treatment with a coupling agent can be assessed by comparing the results of treated and untreated composites.

Lignocellulosic fiber content (%)	Tensile strength (MPa)
without	**HDPE / Lignocellul**
0	28.3
10	27.5
20	24.5
30	20.8
40	21.0
epolene	**HDPE / Lignocellu**
0	28.3
10	26.7
20	24.5
30	23.7
40	24.5
silane	**HDPE / Lignocell**
0	28.3
10	30.2
20	33.1
30	37.9
40	44.5

The tensile strength clearly decreases as the lignocellulosic fiber content increases, in both untreated and epolene treated composites. However the decrease is significantly greater in untreated composites (25%) than it is in epolene treated composites (13%). Therefore, the use of epolene certainly enhances the adhesion capacity at the interface. The composites treated with silane show a completely different behavior because the tensile strength considerably increases when lignocellulosic fibers are present (i.e. there is an increase in tensile strength of 57% when incorporating 40% of lignocellulosic fibers). Consequently, both the lignocellulosic fiber content and the nature of the coupling agent used influence the tensile strength.

Lignocellulosic fiber content (%)	Tensile strength (MPa)	Young modulus (MPa)
without	**HDPE / Lignocellulosic fiber composites v**	
0	28.3	1470
10	27.5	2190
20	24.5	2410
30	20.8	2590
40	21.0	3070
epolene	**HDPE / Lignocellulosic fiber composites**	
0	28.3	1470
10	26.7	1804
20	24.5	2330
30	23.7	2750
40	24.5	3230
silane	**HDPE / Lignocellulosic fiber composite**	
0	28.3	1470
10	30.2	1820
20	33.1	2330
30	37.9	2614
40	44.5	3190

Young modulus greatly increase as the proportion of lignocellulosic fibers rises, being independent of the coupling agent used. In all cases (untreated and treated composites), the Young modulus increased by 110 120% when incorporating 40% of lignocellulosic fibers. This mechanical property depends on the dispersion of lignocellulosic fibers in the HDPE matrix, since the lignocellulosic fibers are responsible for the decrease of the deformation capacity within the elastic zone. The HDPE matrix provides ductility whereas the lignocellulosic fibers exhibit brittle behavior with a subsequent loss of toughness to the composite material.

Lignocellulo fiber conte (%)	ion at breaking point (%)	Toughness (J)
	upling agent	
0	23.2	0.132
10	2.8	0.058
20	2.65	0.055
30	1.9	0.025
40	1.6	0.022
	ith epolene	
0	23.2	0.132
10	5.3	0.085
20	3.5	0.035
30	2.3	0.025
40	1.5	0.022
	ith silane	
0	23.2	0.132
10	6.2	0.123
20	5.7	0.067
30	5.4	0.111
40	4.1	0.085

The elongation at breaking point mainly depends on the lignocellulosic fiber content, even though composites treated with coupling agents show slightly better results. This mechanical property decreases from 23.2 to 2.8% (8 times lower) when incorporating only 10% of untreated lignocellulosic fibers. In the case of treated lignocellulosic fibers, the elongation at breaking point is 4 times lower (for both coupling agents). At lignocellulosic fiber contents higher than 20%, there is not a significant difference of elongation for untreated and epolene-treated composites. Silane-treated composites show, however, a better performance. For example, for composites with 40% of lignocellulosic fibers, the elongation at breaking point is twice as much when silane is used compared to untreated and epolene-treated composites.

Lignocellulosi fiber content (%)	**Toughness (J)**
0	0.132
10	0.058
20	0.055
30	0.025
40	0.022
0	0.132
10	0.085
20	0.035
30	0.025
40	0.022
0	0.132
10	0.123
20	0.067
30	0.111
40	0.085

Toughness is another variable highly influenced by the lignocellulosic fiber content. At low lignocellulosic fiber content, the use of a coupling agent (both epolene and silane) is beneficial. For example, when incorporating 10% of lignocellulosic fiber content, toughness is reduced by 56% for untreated materials whereas this value is only 36% and 7% lower when epolene and silane are used, respectively. On the other hand, at higher lignocellulosic fiber content, there are no differences between untreated and epolene-treated materials. When incorporating 40% of lignocellulosic fiber to HDPE, toughness drops from 132 to 22 mJ (6 times lower) for both materials. However, the silane treatment leads to a higher toughness value (85 mJ compared to 22 mJ).

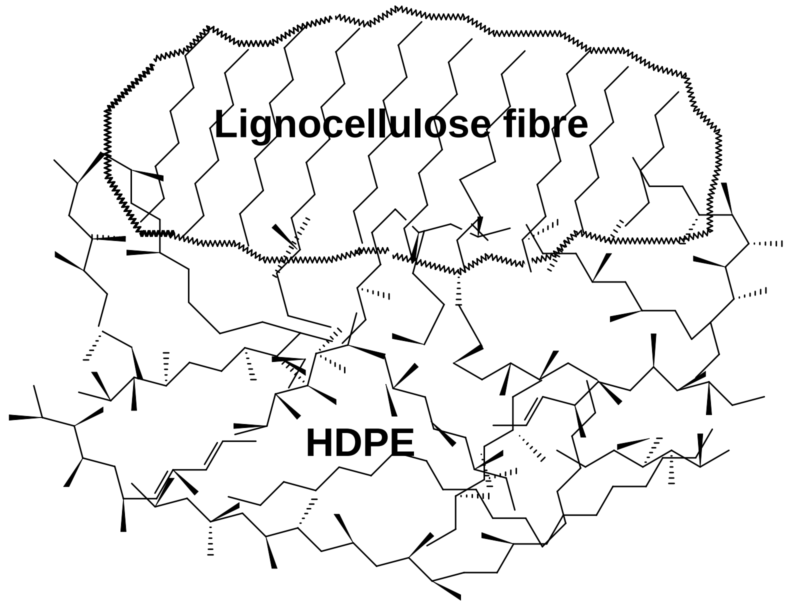
results and discussion

The mechanical properties and the results obtained by FTIR and SEM clearly demonstrate the existence of interactions among the components of the composites (i.e. HDPE matrix and lignocellulosic fibers). The differences observed between the various composites studied (without coupling agent, with epolene and with silane) can be explained by means of particular adhesion mechanisms.

results and discussion

Adhesion mechanisms

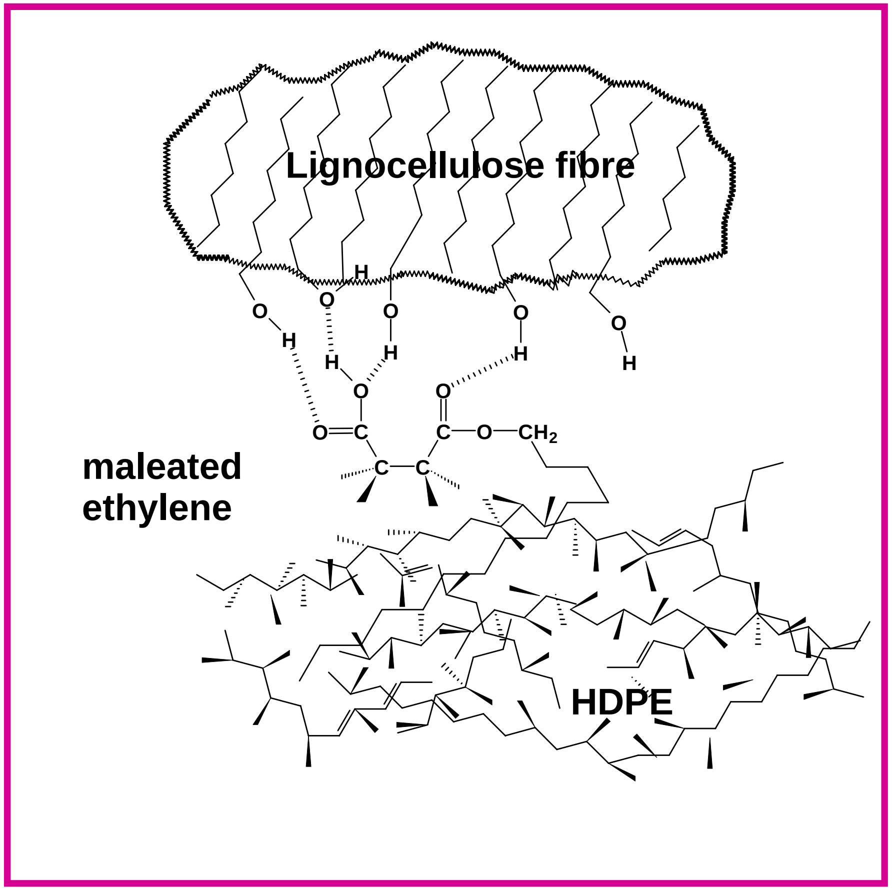
The untreated composites present a very weak physical-mechanics adhesion (better known as interdiffusion) that allows a kind of union between two polymeric surfaces via diffusion of the macromolecules of both polymers



results and discussion

Adhesion mechanisms

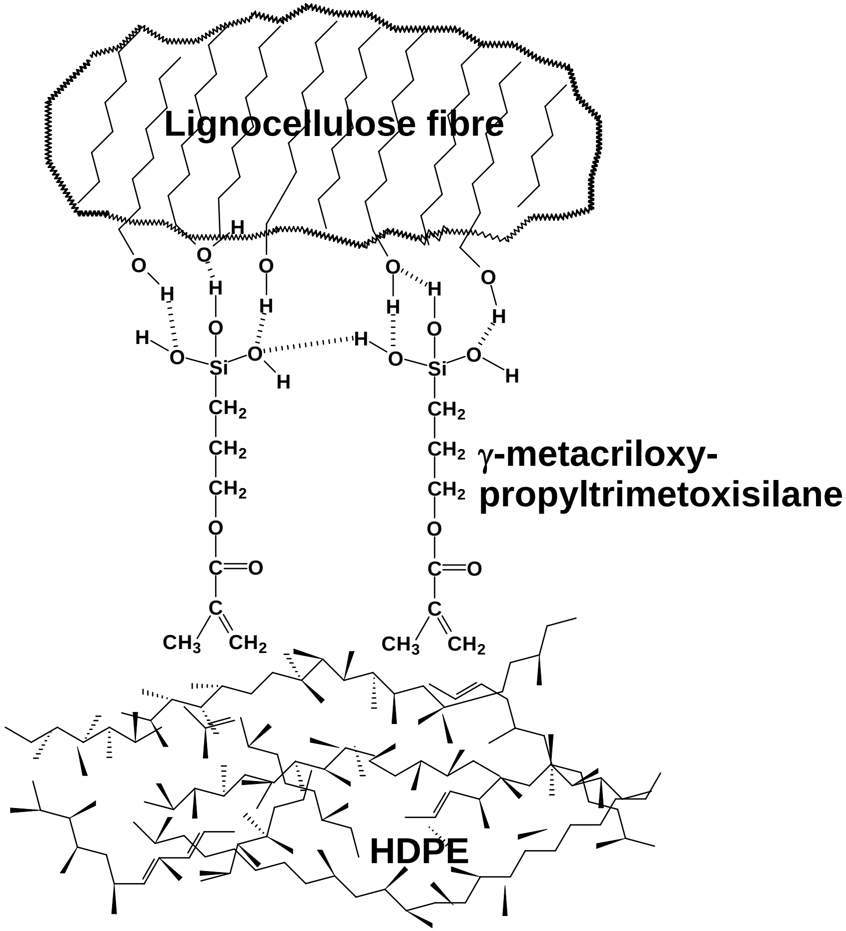
In composites modified with epolene, the presence of groups that can be self-hydrolyzed defines a multiple mechanism of adsorption-wettability, interdiffusion and, to a lesser extent, chemical bonds formed basically by secondary bonding



results and discussion

Adhesion mechanisms

The composites treated with silane show a chemical mechanism of adhesion, with the formation of covalent bonds and also hydrogen bridges, although neither interdiffusion nor adsorption–wetting mechanisms should be excluded



conclusions

By studying the FTIR spectral bands, the main results obtained were the following:

- Water absorption (1635 cm-1) is greater in untreated composites. This means that coupling agents have a protective effect against the penetration of water.
- Epolene interacts more weakly with the glycosidic bond of cellulose (1386 cm-1) than silane.
- The hydroxyl groups of cellulose (1332 cm-1) react with the hydroxyl groups of silanol (coming from the hydrolysis of silane) as well as with the hydroxyl groups produced by the hydrolysis of the anhydride groups in epolene. In both cases, an ether bridge (1162 cm-1) is formed. The silane has a higher capacity to form this covalent bond, thus explaining the higher mechanical performance of silane-treated composites.

conclusions

- The vinyl groups of HDPE react with the double bonds within the coupling agents.
- All these results clearly indicate that the macroscopic properties of the composite materials must depend on the lignocellulosic fiber content and whether or not a coupling agent is used.
- SEM micrographs of fracture surfaces show that the addition of coupling agents enhances their dispersion in the continuous HDPE phase.
- They also show that the silane coupling agent facilitates the direct contact between the lignocellulosic fibers and HDPE matrix more than untreated and epolene treated composites do.
- The tensile strength depends on both the lignocellulosic fiber content and the type of coupling agent used.

conclusions

- The other mechanical properties (Young modulus, elongation at breaking point and toughness) mainly depend on the lignocellulosic fiber content and, to a lesser extent, on the presence of a coupling agent. Silane-treated composites show the best mechanical performance as a consequence of significant interactions at the interface between the HDPE matrix and the lignocellulosic fibers.
- The differences observed between the various composites studied are explained by means of different adhesion mechanisms. Interdiffusion takes place in untreated composites; multiple mechanism of adsorption-wettability, interdiffusion and, to a lesser extent, chemical bonds take place in epolene treated composites, and finally, the adhesion in composites modified with silane is mainly a chemical mechanism of covalent bonds.

any question ?

SURFACE TREATMENT IN REUSED TYRES TO IMPROVE THE INTERFACIAL ADHESION IN POLYOLEFINE MATRIX COMPOSITES

Submmited to Advanced Composites Letters

Prof.   Xavier Colom

Introduction

Used tyres are a major problem in Europe. Used tyres and end of life (EOL) tyres are those tyres, which have completed their functional life and cannot be used for fitment in any automobile. Until recently, they were either buried with other industrial waste in landfill sites or stock piled in huge dumps that could easily contain millions of tyres. It has been estimated that around one billion tyres are withdrawn from use in the world each year. The corresponding Europe is around 250 million tyres. Of these tyres, around 60% are recovered in some way and the rest end up in landfills. Currently, there are different recuperation routes: as reuse, rethreading, recycling, landfill engineering and energy recovery. The European Tyre Recycling Association together with the European Committee for Standardisation has initiated a project aimed to develop common standards for four materials made from used tyres.

aim

- In this paper we propose a new composite material made up from a polyolefine matrix and reinforced with reused tyre as another way to reduce the stock of tyres.

- To improve the interaction between both components, different chemical acids as H_2SO_4, HNO_3 and $HClO_4$. were used as rubber surface modifiers.

- The effect of chemical and physical modification of the surface of tyre reused rubbers on the composite performance has been followed by Mechanical Properties, FTIR, and scanning electronic microscopy (SEM).

experimental part

materials used

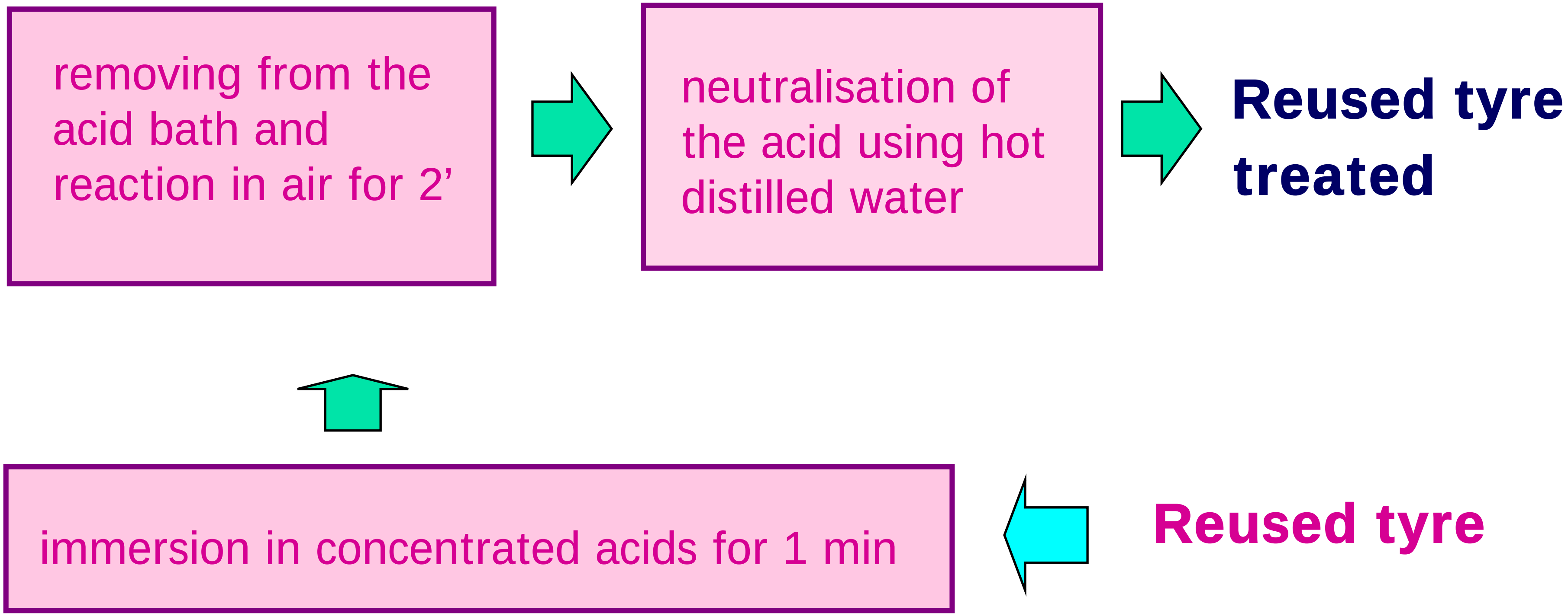
HDPE 2909 supplied by REPSOL-YPF, melt flow index = 1.35 g/min, density = 960 kg/m3

Reused tyres supplied by Alfredo Mesalles-Spain micronized (400 – 600 μm average particle size)

Oxidants acids Three oxidant acids H2SO4, HNO3 and HClO4 were used as a reagents for pretreatments on rubber.

experimental part

Pretreatment of micronized rubber with oxidants acids



removing from the acid bath and reaction in air for 2’

neutralisation of the acid using hot distilled water

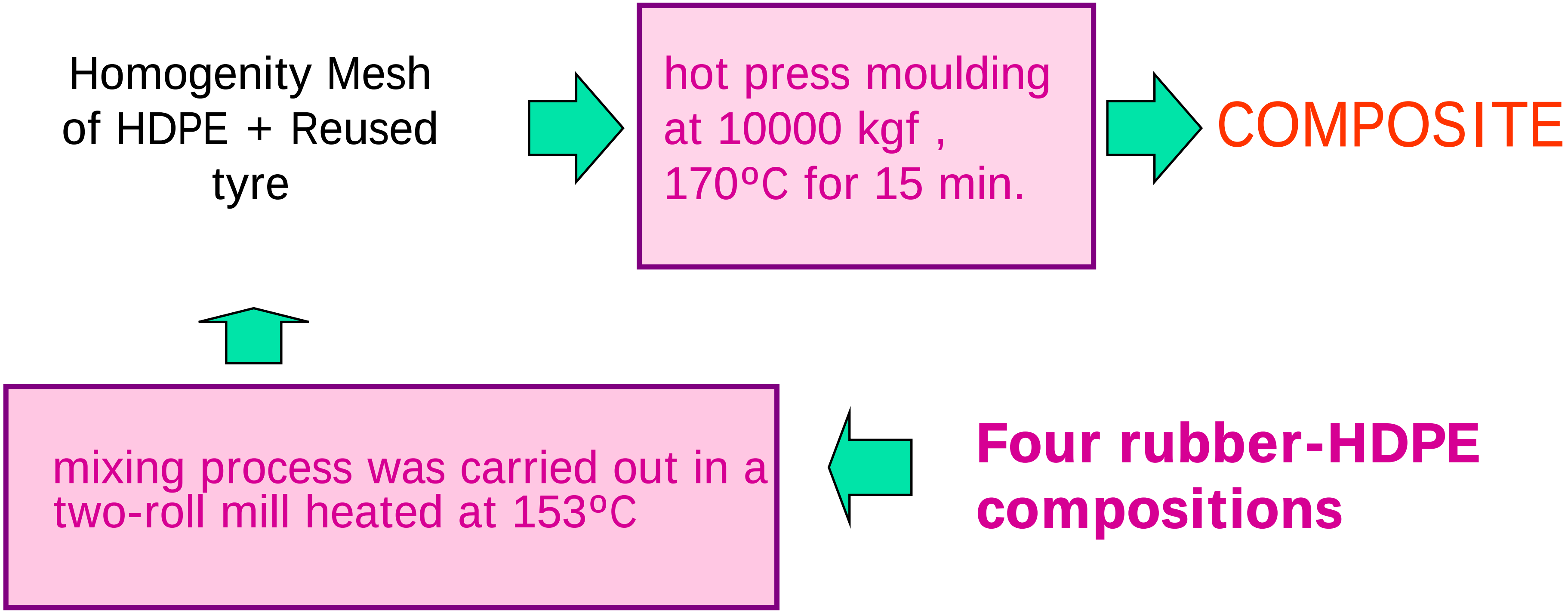
Reused tyre treated

immersion in concentrated acids for 1 min

Reused tyre

experimental part

how to make this composites



Homogenity Mesh
of HDPE + Reused
tyre

hot press moulding
at 10000 kgf ,
170°C for 15 min.

COMPOSITE

mixing process was carried out in a two-roll mill heated at 153°C

Four rubber-HDPE compositions

experimental part

mechanical testing

In each series, a minimum of six samples were tested according to ASTM D-638 procedure. The full-scale load was 5 KN and the cross-head speed was 10 mm/min. The test results were automatically calculated by a HP 86B computing system using Instrom 2412005 General Tensile Test Program.

experimental part

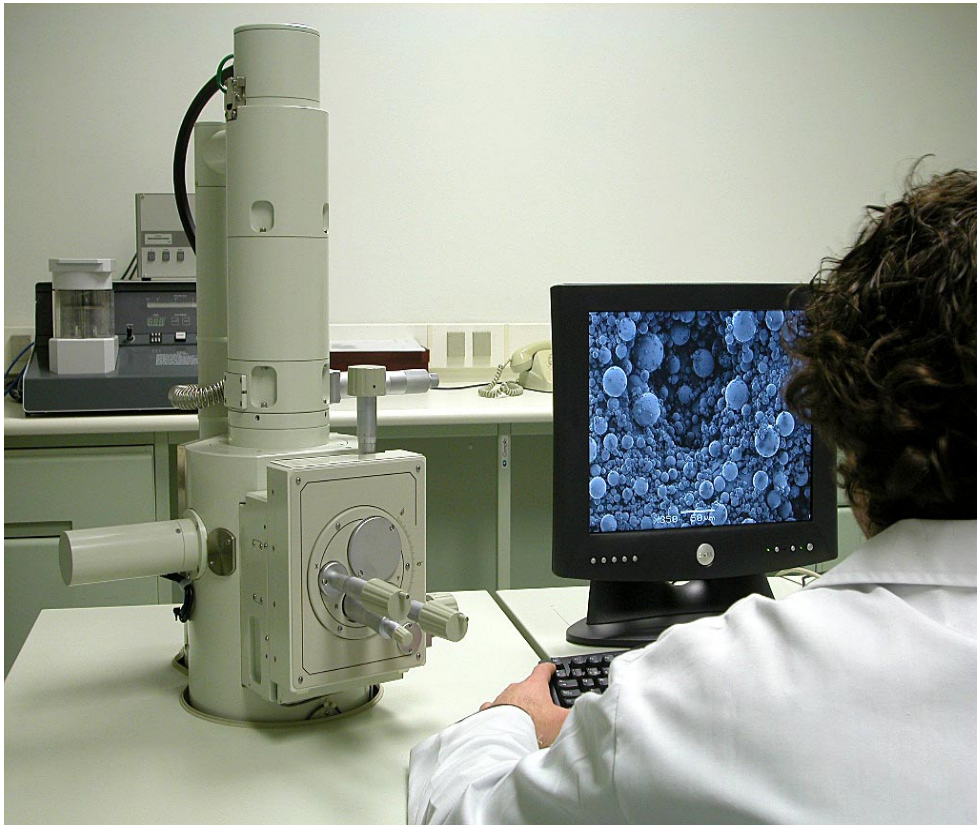
Spectrophotometry FTIR

FTIR spectra were obtained by means of a Nicolet 510 M spectrometer with CsI optics. Samples of the material surface, 9 mg finely divided, were ground and dispersed in a matrix of KBr (300 mg), followed by compression at 167 MPa to consolidate the formation of the pellet. Reduced absorbance values were used in order to avoid the spectral differences arising from the preparation of KBr pellets.

experimental part

Scanning electron microscopy

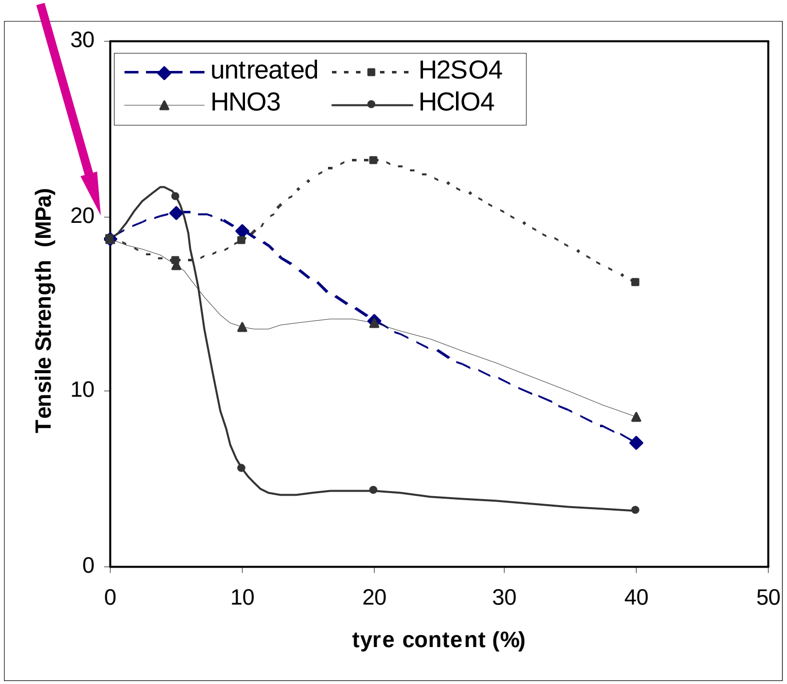
(SEM) was used to examine qualitatively the dispersion and adhesion at the interface between reused tyre and polyethylene matrix. The surface of molded composites was examined with a Zeiss DSM 960 scanning electron microscope. Dry samples were coated with a thin layer of carbon before observation under the microscope, in order to increase the sample conductivity.



results mechanical properties

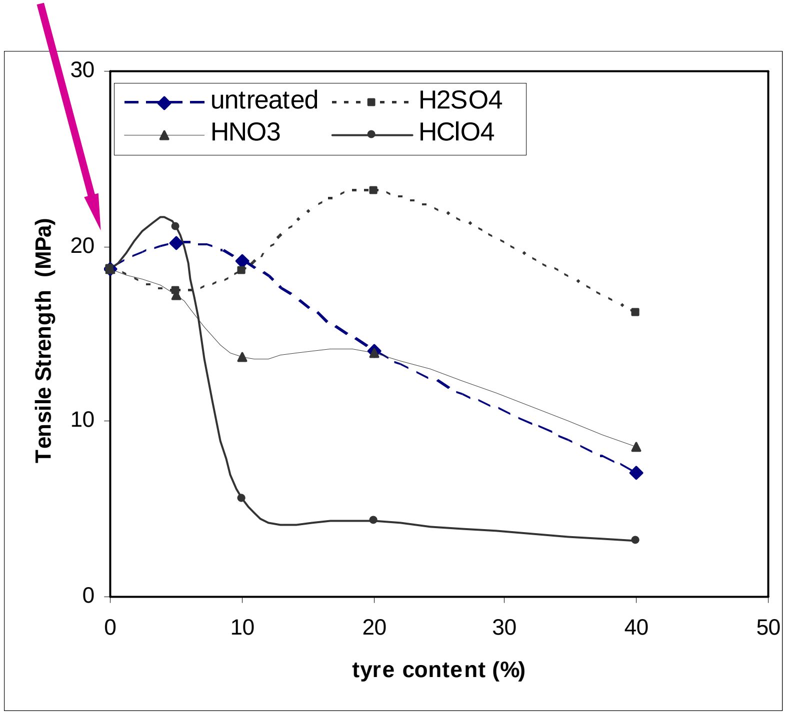
The Tensile Strength of untreated composites generally decrease as the reused tyre content increases. It is further noted that, in comparison with the neat polymer, the tensile strengths of treated composites only improve with increasing reused tyre content in composites where the reused tyre surface is treated with H2SO4. By contrast, the decrease is significantly greater in HClO4 treated reused tyre surface (RTS) composites than it is in HNO3 RTS and untreated composites. Therefore, the use of HClO4 certainly reduce the adhesion ability and the physical contact at the interface.

neat



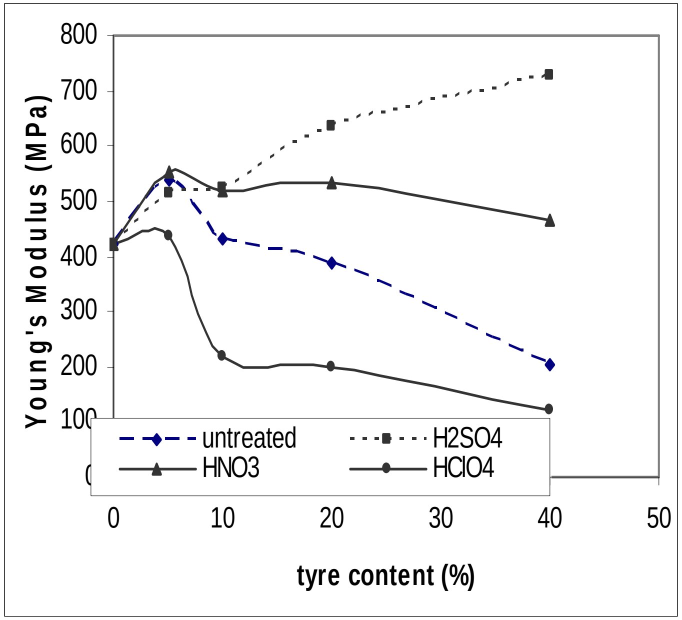
results mechanical properties

The RTS composites treated with H2SO4 show a completely different behavior because the Tensile Strength increases slightly when the filler component is present (i.e. there is an increase in tensile strength of 24% when incorporating 20% of reused tyre). Consequently, both the reused tyre content and the chemical modificator agent used influence on the Tensile Strength. Anyway, it can be seen that for contents of 40% of reused tyre, all composites have a poorer behaviour regarding to Tensile Strength than neat HDPE.



results   mechanical properties

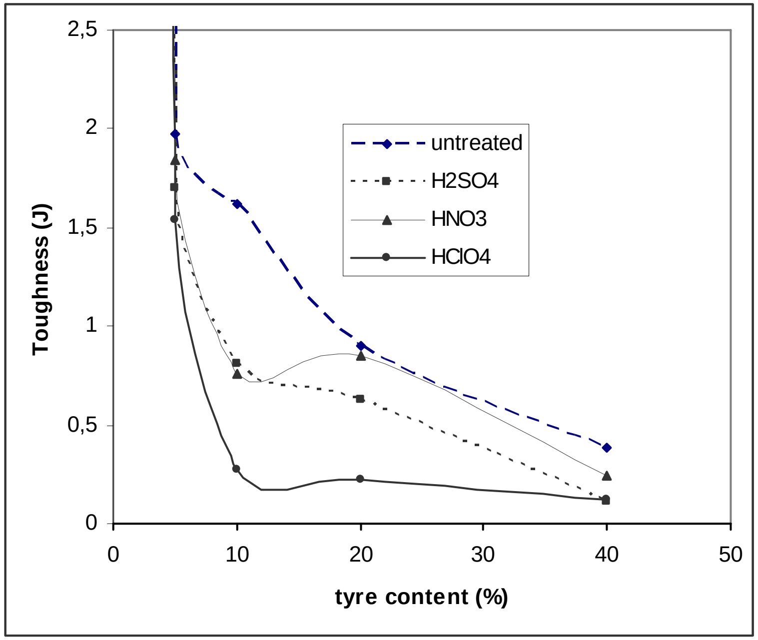
The effect of the modified surface reused tyre on the Young’s Modulus of composites is showed in Figure . In general, the Young’s Modulus for all composites increase only when content in reused tyres is about 5%. Nevertheless, this initial behavior is followed by different tendencies according to the treatment applied. H_2SO_4 and HNO_3 treatments provide a Young’s modulus higher than the value of neat HDPE and the corresponding values of untreated rubber composites, while the treatment with $HClO_4$ obtains lower results, compared either with HDPE or with composites made with untreated rubber The increase achieved with H_2SO_4 is far higher than with HNO_3 (73% in front 11% when incorporating 40% of reused tyre).



results mechanical properties

The different mechanical properties depends on the dispersion of reused tyre in the HDPE matrix.

Differently from other toughened materials, the reused tyre is responsible for the decrease of the deformation capacity within the elastic area. In this case, the HDPE matrix, a very plastic type, provides ductility, whereas the very rigid reused tyre exhibits a brittler behavior with a subsequent loss of toughness in the composite material (figure).

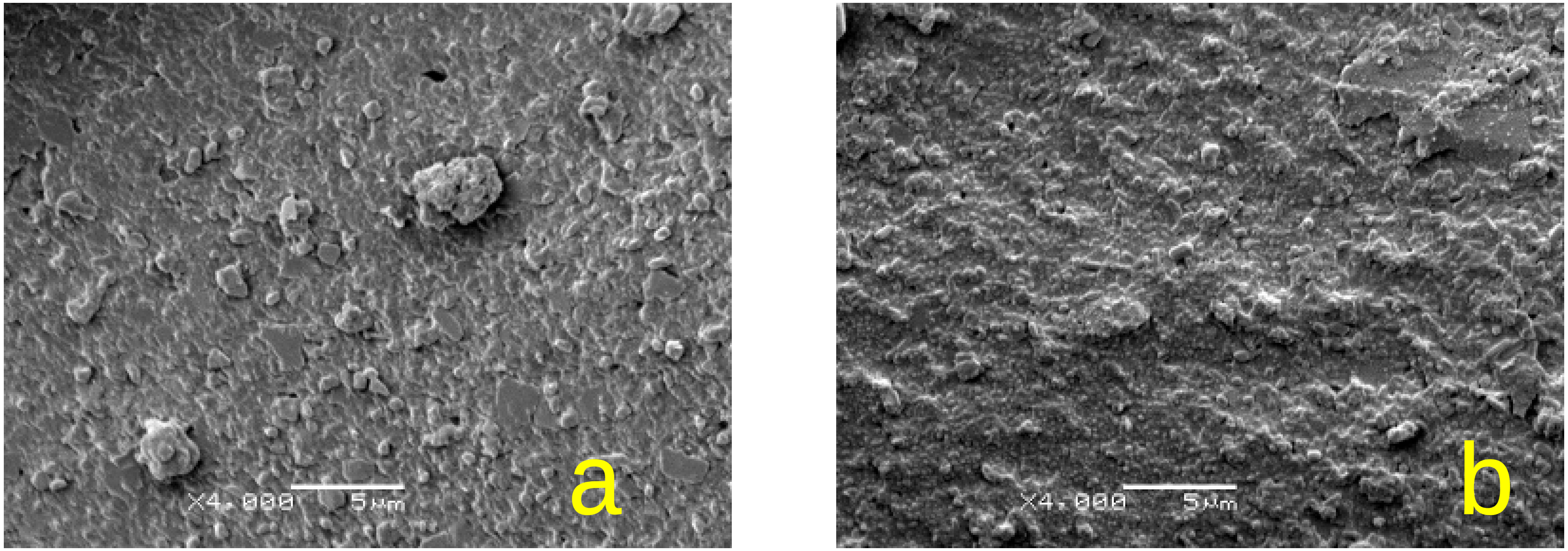


results **mechanical properties**

The elongation at breaking point (figure) mainly depends on the reused tyre content, even though composites made of rubber modified with chemical agents show lower results. This mechanical property decreases from 999 to 41% (25 times lower) when incorporating only 5% of untreated reused tyre. In the case of modified reused tyre, the elongation at breaking point is 34 times lower

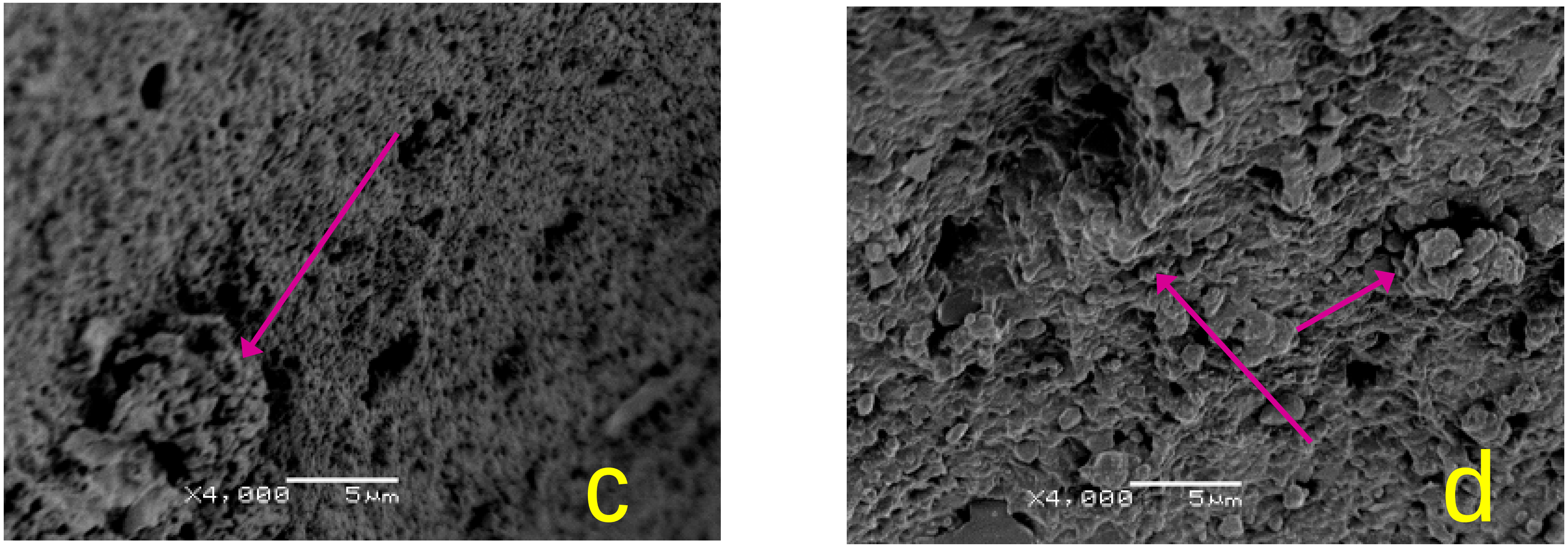
(for all oxidant acids).

results Scanning Electronic Microscopy



Untreated particles (a) show a smooth surface, not apt to mechanic adhesion. $HClO_4$ (b) does not seem to affect intensely surface characteristics. This weak attack may explain the low values in properties of materials submitted to this treatment.

results Scanning Electronic Microscopy



HNO3 (d) and H2SO4 © provide a rough surface, including formation of micropores and cavities that appear as convenient to improve the interfacial contact and the link between matrix and disperse particles

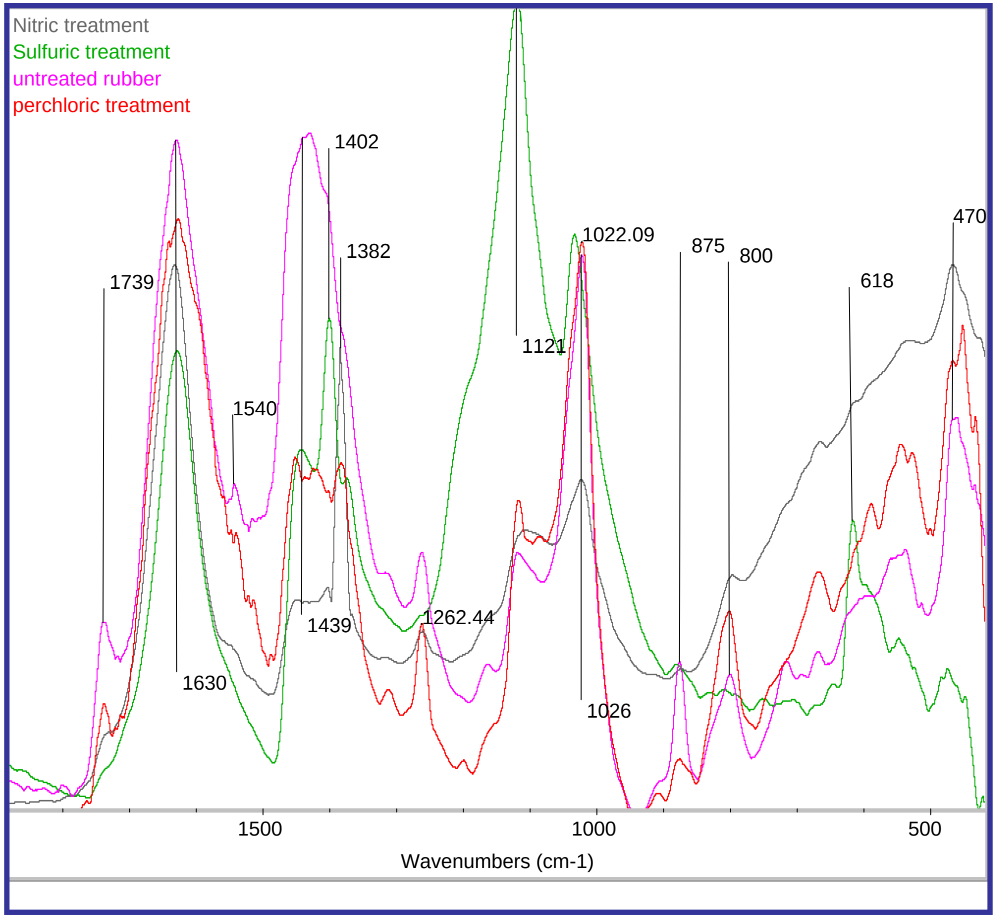
results Scanning Electronic Microscopy

The effect is particularly strong in case of the H2SO4, what is directly related to the performance of the materials obtained with rubber treated with this acid when tested mechanically.

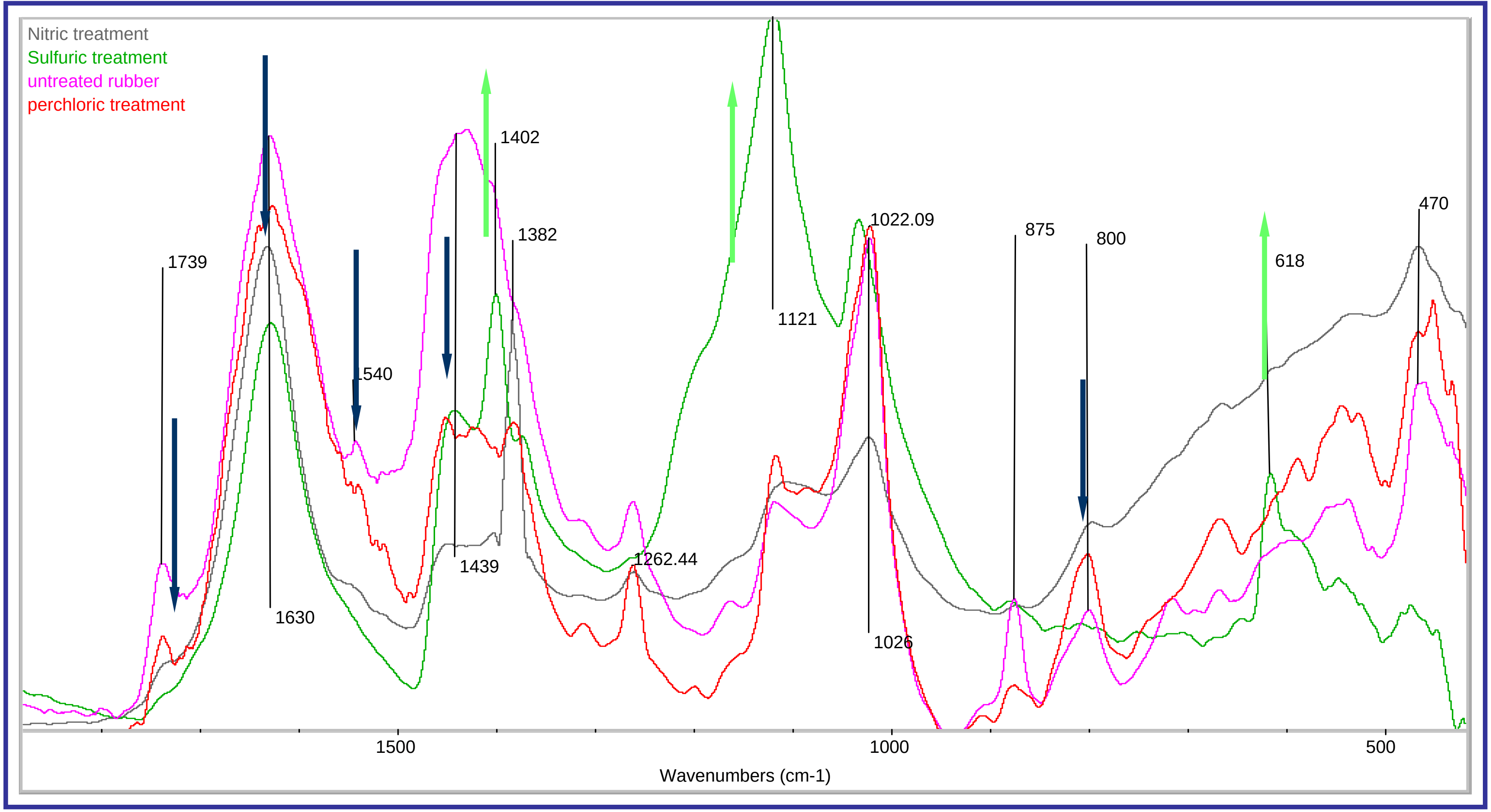
The microroughness achieved by these treatments is related to the ability of the acid to eliminate part of some components on the reused tyre on the surface of the particle.

results Spectroscopy study of surface treatment

To obtain this spectrum we have choosen as a reference the band at 1026 cm-1 assigned to carbon black [6,7]. The spectral analysis of untreated reused tyre shows a weak band at 1739 cm-1 associated with thermo oxidative reactions, due to the exposure of the surface to oxygen, that induces the formation of an oxidation skin that includes carbonyls groups (1). The strong band at 1640 cm-1 is associated to C=C polyisoprene, the weak band at 1540 cm-1 to zinc stearate (antiadherent compound), bands at 1430 C to scissoring vibrations of =CH2 (butadiene), band at 875 cm-1 associated at trans isopropenyl unit (-C(CH3)=CH-) and the band at 470 cm-1 associated at S-S.



results Spectroscopy study of surface treatment



results Spectroscopy study of surface treatment

The study of FTIR spectra shows that the treatment of the tyre rubber with sulphuric acid produced several chemical degradative modifications on the tyre surface, mainly formation of sulphonic acid, decrease of double bonds (1640 cm-1) due to degradation process of polybutadiene and other unsaturated components of tyre and decrease of content in minor components. These phenomena can be related to the disappearing of the weak bands at 1739 and 1540, decreasing of bands at 1430 and 875 and appearing of new bands at 1402, 1121 and 618 cm-1, indicative of O=S=O stretching absorptions of sulphonic acid. This results are in agreement with previous studies by diverse authors. Simultaneously with the chemical modifications, physical changes in the surface as the formation of microroughness, and microporosities observed by SEM at figure 5 are due to the observed partial degradation of some components.

results Spectroscopy study of surface treatment

The treatment of rubber tyre with nitric acid present similar results to the sulphuric acid treatment. As appears at figure, the spectrum of samples exposed to nitric acid action show the decrease of the same bands that in sulphuric acid case (1739, 1640, 1540, 1430 and 875 cm-1) plus an increase of the band at 1382 cm-1 assigned to N-N=O. These spectral similarities are consistent with the resemblance of mechanical and topographical results between samples treated with these acids.

results Spectroscopy study of surface treatment

On the contrary, the spectrum of samples treated superficially with perchloric acid show less intense chemical modifications and a dissimilitude that agree with the observed difference in mechanical performance and physical modifications.

Both microscopy and spectrofotometry results summarized above, suggest that surface modification of tyres with different treatments, influence the mechanical properties and, in some cases, can also improve the interaction and compatibility between HDPE matrix and reused tyre fillers.

concluding remarks

From the study of mechanical properties of the prepared composites, we can conclude that:

1 The addition of micronized reused tyre rubber to the HDPE in small quantities (5%) act as a filler, improving the stiffness and providing a brittler behaviour.

2 Contents of rubber above 10%, using either untreated rubber or HClO4 treatment obtain lower values of Young’s modulus than original HDPE. Elongation values and toughness are also lower. This effect can be attributed to the poor adhesion interfacial between the composite components

concluding remarks

3 Treatments with H_2SO_4 and HNO_3 both improve the interaction ability of rubber with HDPE, providing the materials a higher stiffness that may be also a consequence of the rigidization of the rubber after the acidic treatment because of the extraction of additives and the degradation.

4 The treatment with H_2SO_4 is the most effective, whereas the $HClO_4$ does not improve the materials’ properties

concluding remarks

finally

According to these results, in order to achieve a better mechanical performance in terms of rigidity, the acid sulphuric treatment seems to obtain the best results. Nature and intensity of the chemical modifications together to the surface microrougness that generates on the reused tyre rubber is more suitable for adhesion with the matrix that any other studied treatment.