10-1.- Structural Characterization of different Composites

STUDY OF THE CHANGES IN CRYSTALLINITY OF THE HDPE MATRIX IN COMPOSITES WITH CELLULOSIC FIBRES USING DSC AND FT-IR.

journal of reinforced plastics and composites

Prof. Xavier Colom

aim

- This paper studies the influence of the drastic climatic conditions of the Canadian winter on the changes of crystallinity of the component matrix in HDPE composites/cellulosic fibres.

- Two types of samples have been treated during different periods of time, one in which cellulosic fibres have not been treated, and another, in which fibres have been given a treatment with a coupling agent, silane type, which favours the fibre adhesion to the matrix. A parallel study has been carried out in function of the different percentages of cellulosic fibres of both composites.

experimental part

materials used

HDPE 2909 of Du Pont Canada,

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

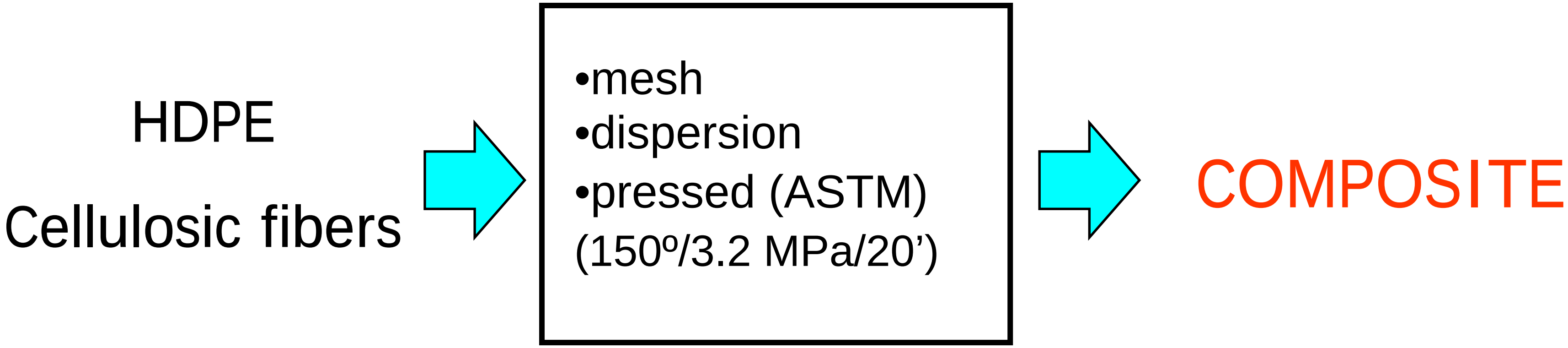
Cellulosic fibres were short fibres of aspen (populus tremula), whose length/diameter ratio is L/D=8,7.

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

experimental part

how to make this composites

without coupling agents



HDPE

Cellulosic fibers

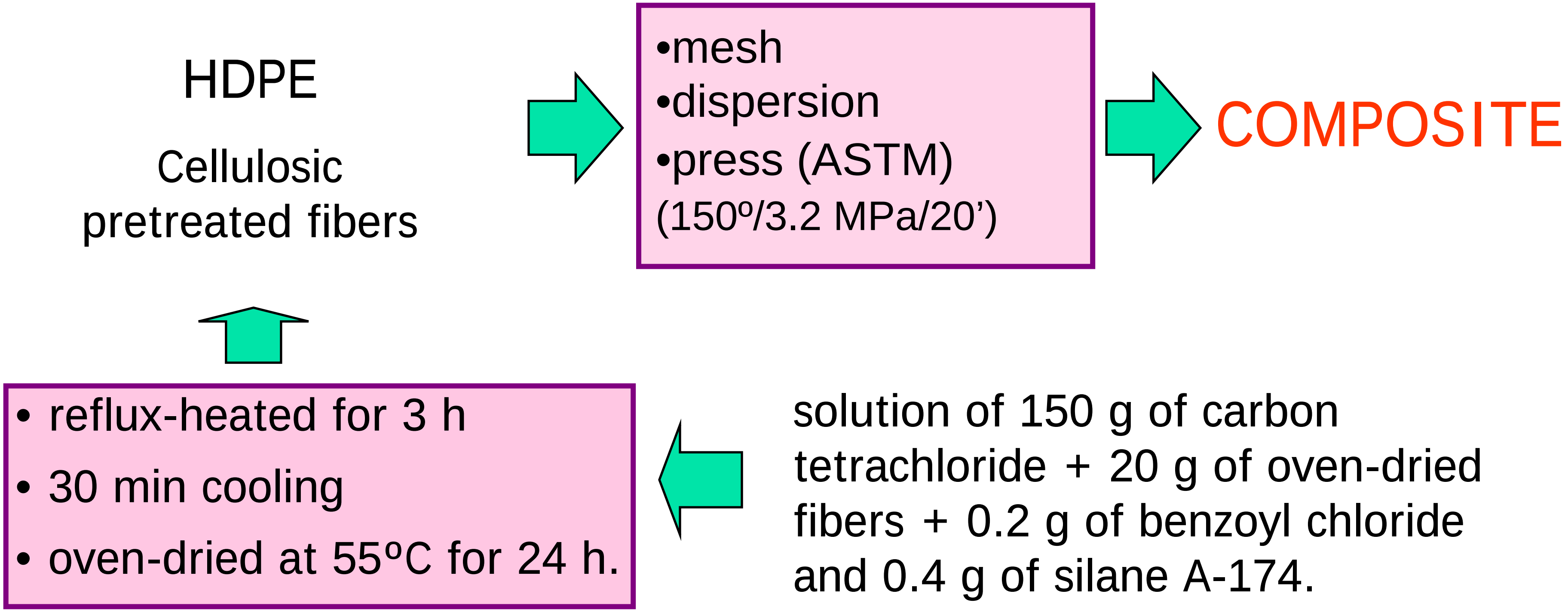
- mesh
- dispersion
- pressed (ASTM) (150º/3.2 MPa/20’)

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

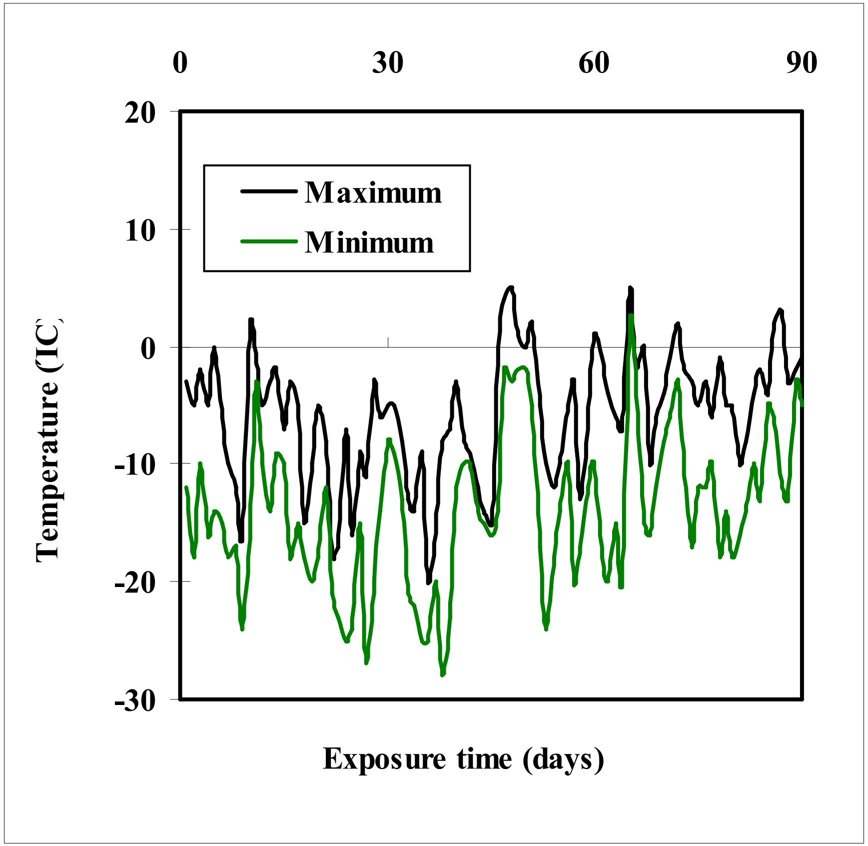
- reflux-heated for 3 h
- 30 min cooling
- oven-dried at 55ºC for 24 h.

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.

Degradation process

Samples of composite were exposed to environmental conditions during different periods of time: 15, 30, 60 and 90 days and, then, kept at a temperature of 20ºC during 20 min. before evaluating their crystallinity.

Figure shows the maximum and minimum temperatures of each day during the exposure time samples



experimental part

Spectrophotometry FTIR

FT-i.r. spectra were obtained in a Nicolet Avatar spectrophotometer, with CsI optics.

To prepare the samples, the method used consisted of dispersing the specimen surface, finely divided (9 mg) in a matrix of KBr (300 mg), followed by compression at 167 MPa so as to consolidate the formation of the pellet.

experimental part

Spectrophotometry FTIR

- To determine crystallinity, the method suggested by Zerbi et al. (11) was used; the spectral bands of doublets (1474-1464 cm-1 and 730-720 cm-1) corresponding to flexural vibrations: 1474 and 730 cm-1 (crystalline phase) and 1464 and 720 cm-1 (amorphous phase) are used.
- Two spectral areas have been basically analysed: 600-800 cm-1 and 1400-1500 cm-1. To obtain the characteristical spectra of HDPE from the own spectra of the different composites the methodology applied is composed of two stages: a) the characteristical spectrum of cellulosic fibres is multiplied by the percentage of fibre in the composite on which crystallinity will be determined, and b) the obtained spectrum is substracted as indicated for the own spectrum of the composite in which the crystallinity of its component matrix will be determined (HDPE).

experimental part

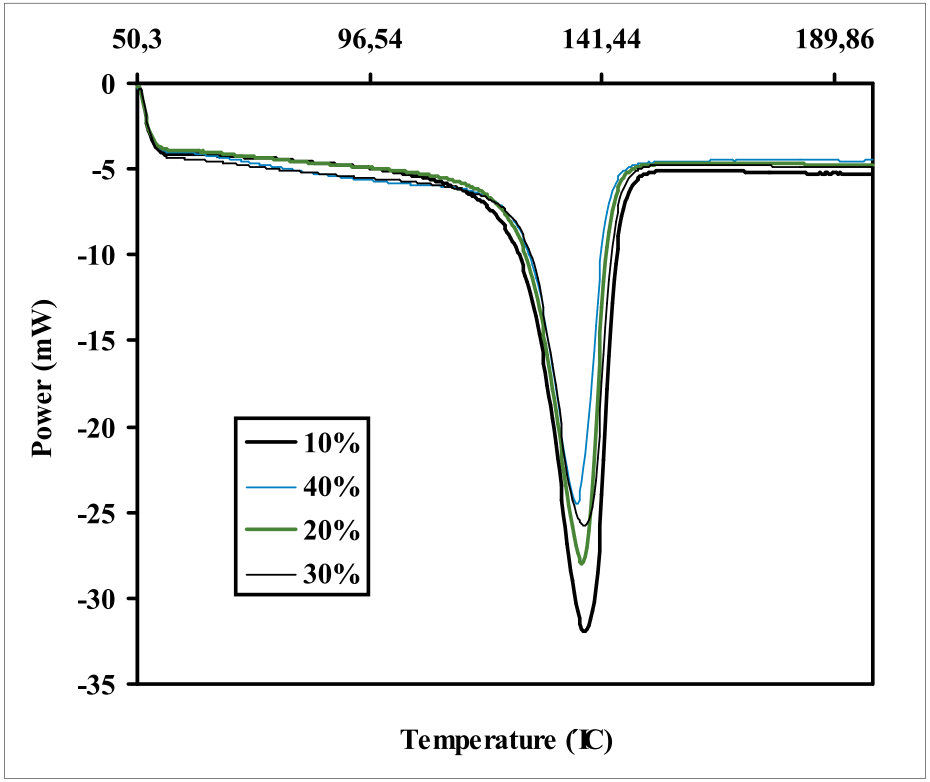
Differential Scanning Calorimetry

A DSC 30 Mettler instrument with liquid nitrogen was used to obtain the thermograms. The sample mass oscillated between 2.0 and 3.0 mg; the mass was small enough to prevent problems caused by heat and material transfer. The heating rate was 10 K/min and the temperature range was between 50 and 200ºC. Calibration of temperatures and energies was made with a standard of In, Pb and Zn under the very same conditions used in the sample analysis

results and discussion

study of crystalinity by DSC analysis

This figure shows different DSC thermograms representing samples of composites without a coupling agend. These thermograms indicate the melting enthalpy (ΔHf). The results are shown in next table.



results and discussion

	HDPE/Cellulosic fibre composites without coupling agent			
Cellulosic fibre content (%)	**Exposure time (days)**	**Melting temperatures (ºC)**	**Melting Enthalpy (J/g)**	**ΔH_f average for each percentage of cellulosic fibres**
10	15	142.3	199.44	200.93 (±3.73)
	60	141.2	199.77	
	90	142.4	203.70	
20	30	141.0	188.77	192.75 (±2.96)
	60	140.0	195.87	
	90	139.1	193.62	
30	60	141.0	186.85	187.21 (±0.43)
	90	142.3	187.71	
40	15	139.6	174.66	176.5 (±2.17)
	60	138.3	179.50	
	90	140.7	175.16	

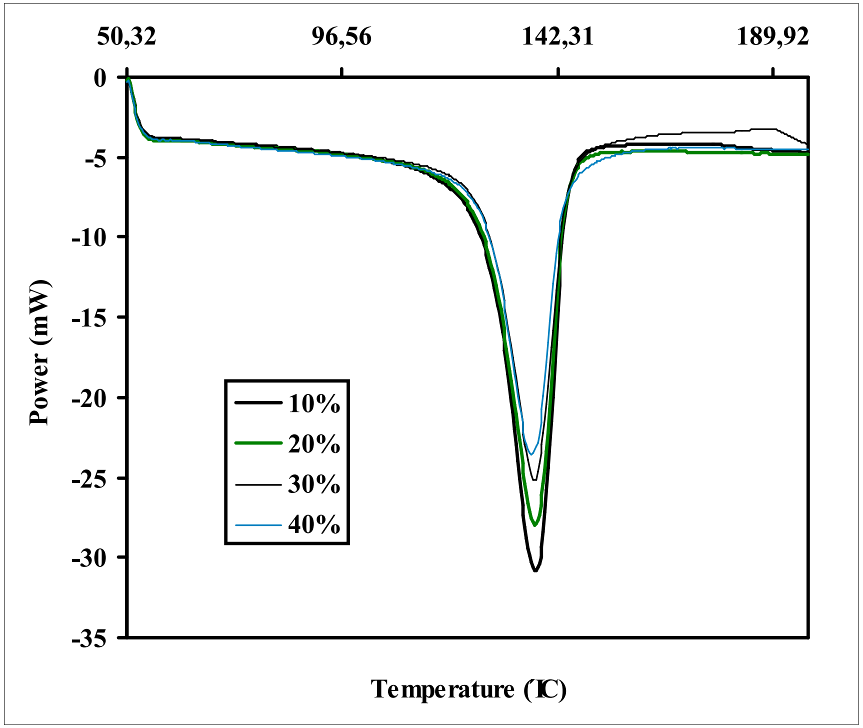
results and discussion

		HDPE/Cellulosic fibre composites without coupling agent					
		730/720 cm^{-1}			1474/1464 cm^{-1}		
Cellulosic fibre content (%)	**Exposure time (days)**	**Ia/Ib**	**Amorphous content (%)**	**Crystalline content (%)**	**Ia/Ib**	**Amorphous content (%)**	**Crystalline content (%)**
10	15	0.7712	21.25	78.75	1.1911	1.57	98.43
	60	0.7701	21.29	78.71	1.1569	2.87	97.13
	90	0.7584	21.99	78.01	1.1890	1.65	98.35
20	30	0.7901	19.99	80.01	1.2910	2.35	97.65
	60	0.7630	21.58	78.62	1.2401	1.96	98.04
	90	0.7661	21.38	78.42	1.2203	0.99	99.01
30	60	0.7481	22.50	77.50	1.3067	2.86	97.14
	90	0.7360	23.23	76.77	1.2930	2.44	97.56
40	15	0.6404	29.30	70.69	1.4824	8.18	91.86
	60	0.6082	31.58	68.42	1.4652	7.48	92.52
	90	0.5522	35.36	64.64	1.5439	9.87	90.13

results and discussion

study of crystalinity by DSC analysis

Figure show different DSC thermograms representing samples of composites with a coupling agent silane A-174. These thermograms indicate the melting enthalpy (ΔH*f*).



results and discussion

	HDPE/Cellulosic fibre composites with silane A-174 as a coupling agent			
Cellulosic fibre content (%)	**Exposure time (days)**	**Melting temperatures (ºC)**	**Melting Enthalpy (J/g)**	**ΔH_f average for each percentage of cellulosic fibres**
10	30 60 90	142.8 138.8 139.1	187.44 191.22 194.66	191.31 (±5.35)
20	60 90	141.0 138.6	192.87 190.75	191.78 (±1.07)
30	30 30	139.6 140.4	190.14 190.09	190.10 (±0.02)
40	30 60 90	140.7 139.6 139.9	191.14 187.66 186.39	188.4 (±3.07)

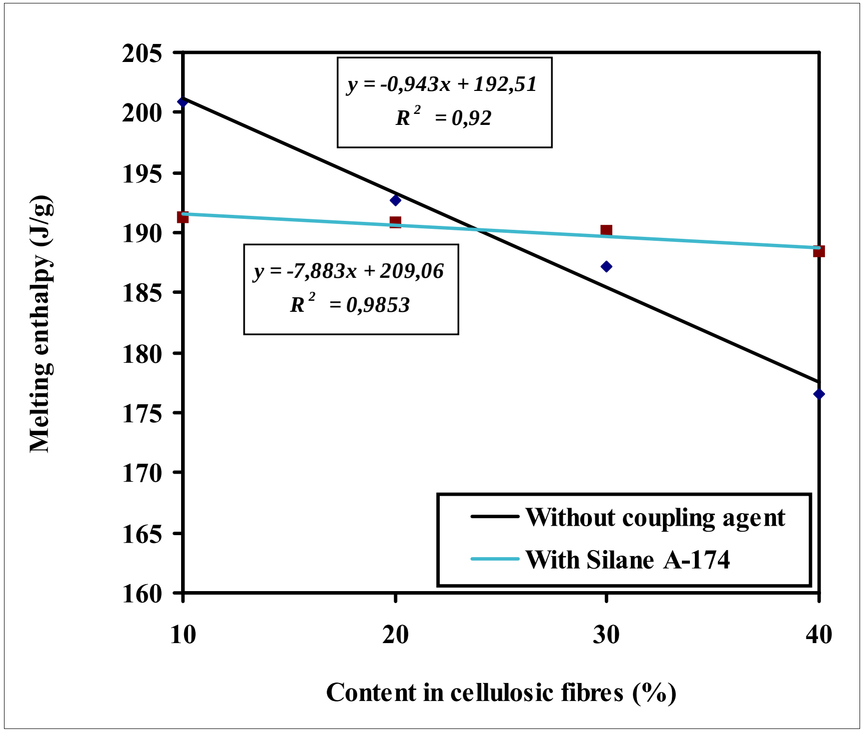
results and discussion

HDPE/Cellulosic fibre composites with coupling agent (silane A-174)							
		730/720 cm^{-1}			1474/1464 cm^{-1}		
Cellulosic fibre content (%)	**Exposure time (days)**	**Ia/Ib**	**Amorphous content (%)**	**Crystalline content (%)**	**Ia/Ib**	**Amorphous content (%)**	**Crystalline content (%)**
10	30	0.8107	19.92	80.07	1.1434	3.50	96.50
	60	0.8181	18.52	81.48	1.1546	2.97	97.03
	90	0.8232	18.23	81.77	1.1783	2.05	97.95
20	60	0.7804	20.47	79.53	1.2270	0.69	99.31
	90	0.7750	20.99	79.01	1.8004	1.97	98.03
30	30	0.7601	21.80	78.20	1.3170	3.00	97.00
	60	0.7552	22.09	77.91	1.3589	4.32	95.68
40	30	0.7751	21.00	79.00	1.3201	2.90	97.10
	60	0.7679	21.34	78.66	1.3623	4.43	95.57
	90	0.7638	21.58	78.42	1.3751	4.84	95.16

results and discussion

study of crystalinity by DSC analysis

Figure illustrates that the variation of the average enthalpy with the percentage of cellulosic fibres is more perceptible when cellulosic fibres have not been pretreated. In such case, when increasing 10 % the content in fibres, the melting enthalpy decreases 8 J/g while it only decreases 1 J/g when fibres have been pretreated with silane A-174.



results and discussion

study of crystalinity by DSC analysis

Results found by DSC demonstrate that the loss of crystallinity in the HDPE matrix in the different samples examined is directly related to the percentage of cellulosic fibres and, also, that no relation exists between the exposure time to environment and the crystallinity loss for the same percentage of fibre.

This result indicates that the presence of the coupling agent largely contributes to the adhesion between the matrix and the reinforcement, as an important variation of the content in fibres causes small modifications in the melting enthalpy.

results and discussion

From the results obtained by FTIR and DSC techniques it is seen that the crystallinity loss of the HDPE matrix in HDPE/cellulosic fibres composites without a coupling agent is caused by:

- Interactions between the HDPE/cellulosic fibres components in their own interface producing microstructural conformation changes in the crystalline structure of the HDPE.

- The ability of the highly hygroscopic cellulosic fibres to take up and retain water molecules due to the aggressive weather conditions with high humidity. The accumulative effect of the fibrous reinforcement in direct contact with the HDPE matrix causes microstructural changes that notably affecting its crystallinity.

results and discussion

- It is also observed for each different percentage of fibre that any direct relation between the crystallinity loss and the exposure time of samples doesn’t exist.

- This fact is due to the same absorption-desorption phenomenon of the cellulosic fibres which can, in a certain way, regulate the transfer of water molecules from inside the fibres to the HDPE / cellulosic fibres interface, causing extent losses of crystallinity irrespective of the exposure time.

- Composites treated with silane A-174, cellulosic fibres also originate a crystallinity decrease although the presence of a coupling agent makes crystallinity practically independent of the fibre percentage.

results and discussion

- The loss of crystallinity is almost exclusively induced by the interactions being generated between the coupling agent and the components of the composite.

- Silane A-174 improves the adhesion between the components of the materials that define a protective effect which prevents the contact between environment-cellulosic fibres and avoids, to a large extent, the humidity absorption of the fibrous reinforcement

- Therefore, the loss of crystallinity of the HDPE matrix caused by the environmental exposure conditions will be rather similar to that undergone by pure HDPE

conclusions

- This degradation is revealed by a progressive decrease of the component matrix owing to the environmental exposure conditions.

- The conditions on which composites have been exposed affect the HDPE matrix in a different way in function of the type of treatment.

- The loss of crystallinity of the HDPE matrix is directly related with the percentage of cellulosic fibres, being much more perceptible in the case of samples without a coupling agent

STUDY OF MISCIBILITY OF POLY(E-CAPROLACTONE)-POLY (VINYL CHLORIDE) BLENDS, BY FT-I.R. SPECTROPHOTOMETRY.

journal of polymer materials

Prof. Xavier Colom

aim

This paper studies miscibility of blends of polymers using the FTIR spectroscopy technique. Blends of poly(e-caprolactone) and poly(vinyl chloride) were previously characterised through techniques of spectral substraction plus observation of the spectra attained at various temperatures. A different experimental method has been used which consist of comparing the spectra of blends of different proportions in solid state with the theoretical spectra simulated from the component polymers.

experimental part

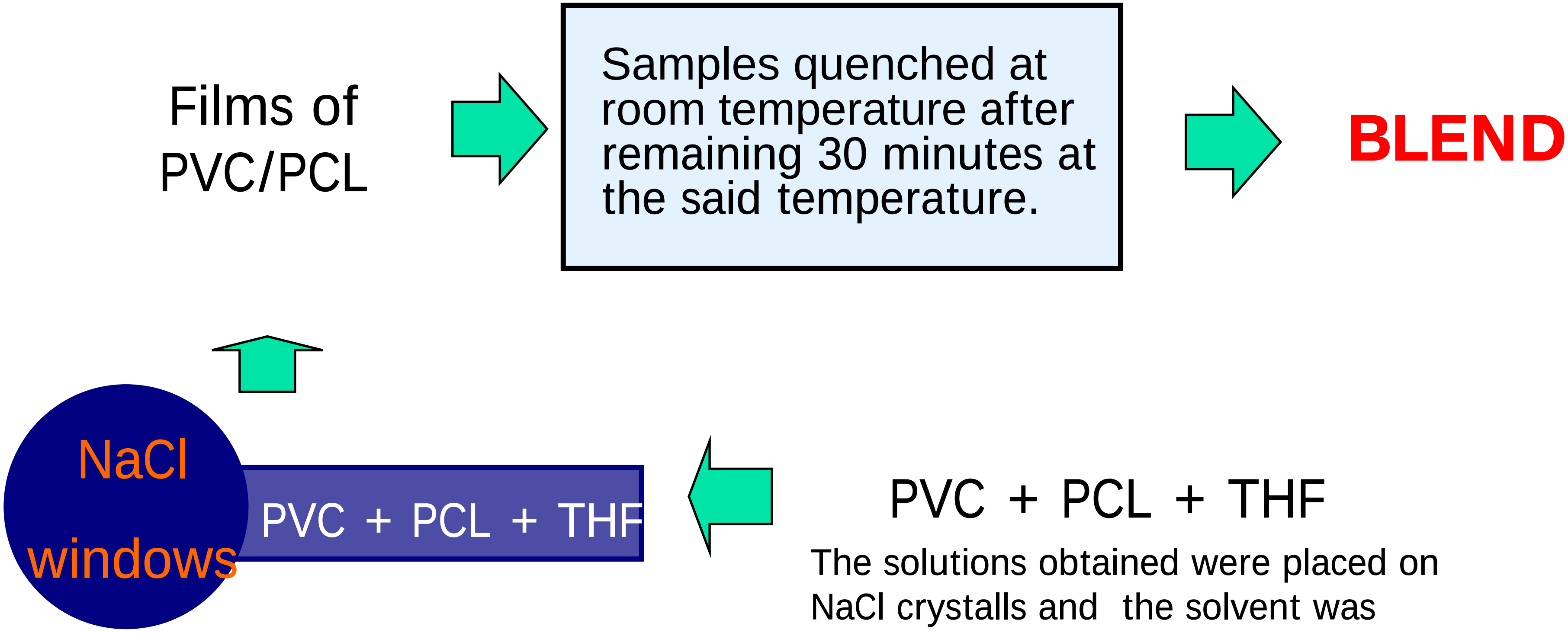
materials used

Polymers (PVC and PCL) have been supplied by Sigma-Aldrich. PVC samples with different PCL percentages 0%, 25%, 50%, 75%, 100% were prepared.

experimental part

Blends were made by dissolving polymers in the adequate ratios in tetrahydrofuran (THF).

how to make this blends



Films of PVC/PCL

Samples quenched at room temperature after remaining 30 minutes at the said temperature.

BLEND

NaCl windows

PVC + PCL + THF

PVC + PCL + THF

The solutions obtained were placed on NaCl crystalls and the solvent was evaporated by heating the surface with an infrared lamp.

experimental part

Spectrophotometry FTIR

- A Nicolet 510 M spectrophotometer was used and spectra were obtained with 200 scans and 2 cm-1 resolution.

- Spectra of these samples were compared with others from PCL and PVC blends in which the existence of any interaction between the two polymers was impossible. The preparation of these spectra, acting as a reference in this study, was carried out from pure PCL and PVC spectra. They have been multipled by the factors convenient to the percentage to be simulated and they have been added up point by point.

results and discussion

- The study mainly focuses the comparison among the sample spectra obtained from the film and (simulated ones) those representing the weighted addition of the spectra of the component polymers.

- Differences between both types of spectra are caused by the interaction between the two polymeric components.

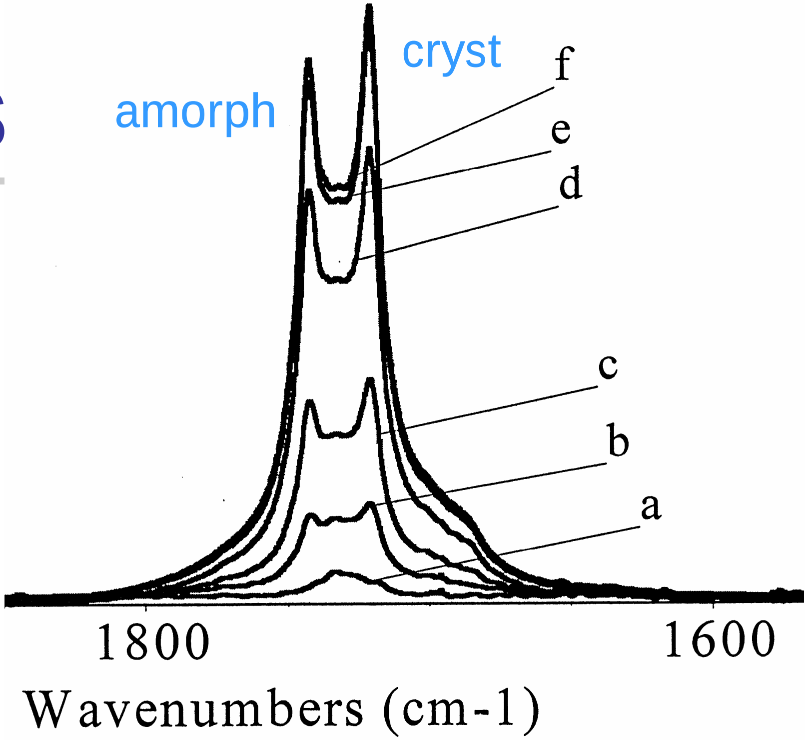
- Two zones have been preferably studied: one corresponding to the carbonyl group, placed in the interval 1720-1745 cm-1, and the other in the interval 1100 - 1300 cm-1, where a great number of wavelengths related with crystallinity are placed.

results and discuss

FTIR of carbonyl group

In the region assigned to the carbonyl group. Two wavelengths are placed at 1742 and 1721 cm-1 associated to tension vibration frequencies of the carbonyl group in the amorphous and crystalline phases, respectively. Figure shows the theoretical spectra of blends which result from adding one by one the spectra of the component polymers in the adequate ratios.

Simulated spectra of blends in the zone of carbonyl group:

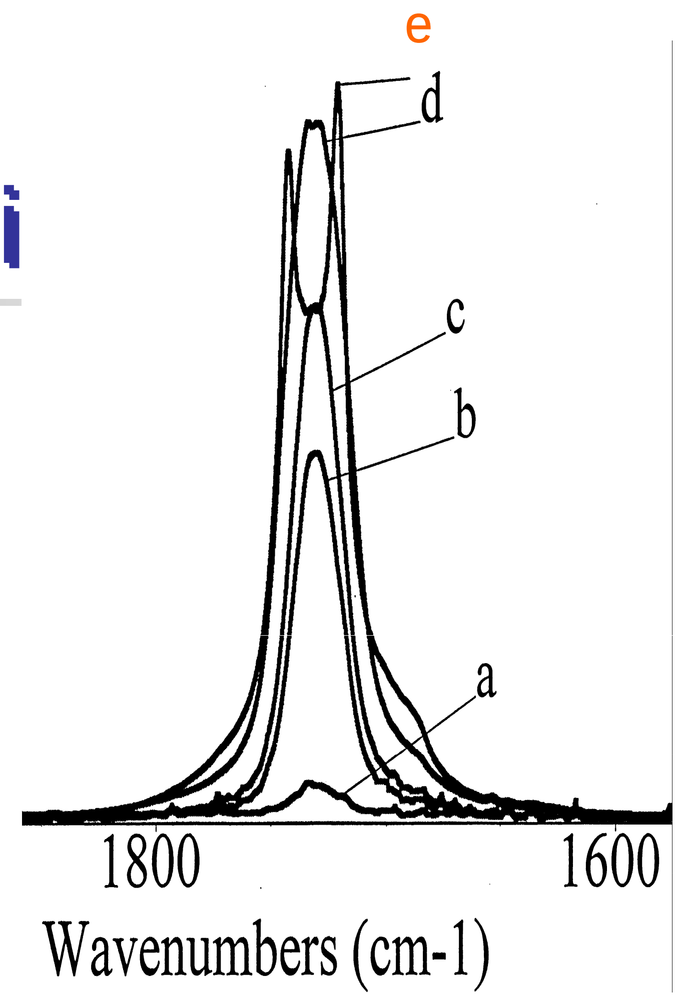


a) PVC film; b) simulations PCL/PVC, 10%; c) simulations PCL/PVC, 35%; d) simulation PCL/PVC, 50%; e) simulation PCL/PVC, 75%; f) PCL film.

results and discussi

FTIR of carbonyl group

The figure attained from films are showed.
While in the simulated spectra of blends, a progressive growth of the carbonyl group bands is observed, in the film blends bands of 1742 and 1721 tend to get together and displacement occurs at a wavenumber around 1730 cm-1

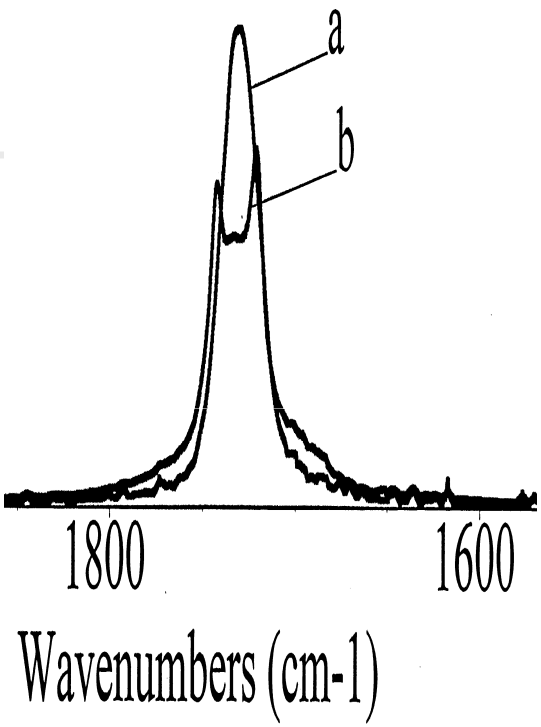


Spectra of blends in the zone of the carbonyl group: a) PVC film; b) PCL/PVC, 10%; c) PCL/PVC, 25%; d) PCL/PVC, 50%; e) PCL film

results and discussion

In Fig a simulated spectrum is compared with the real one of the same ratio; in this figure the difference between them can be more clearly seen.

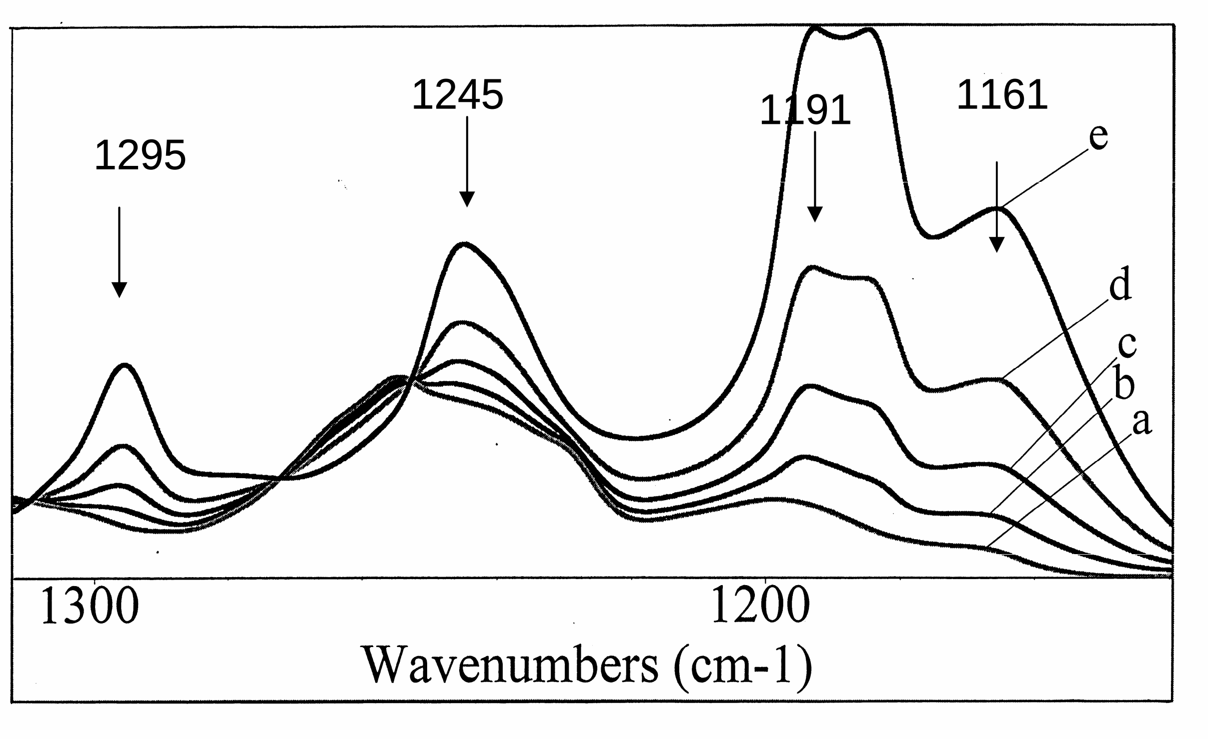
These displacements indicate that PCL carbonyl groups are in the blend in associations that are different from those in amorphous and crystalline state, these new associations are related with the interactions established with PVC. Displacements of bands occur significantly even for low PVC concentrations, and at low concentrations, the most perceptible differences between the simulated and real spectra are observed. This fact could be in relation with a saturation effect from PVC concentrations higher than 60%.



Comparison between the theoretical spectrum of the blend and the real spectrum in the zone of the carbonyl group: a) PCL/PVC, 25%; b) simulation of PCL/PVC, 25%.

results and discussion

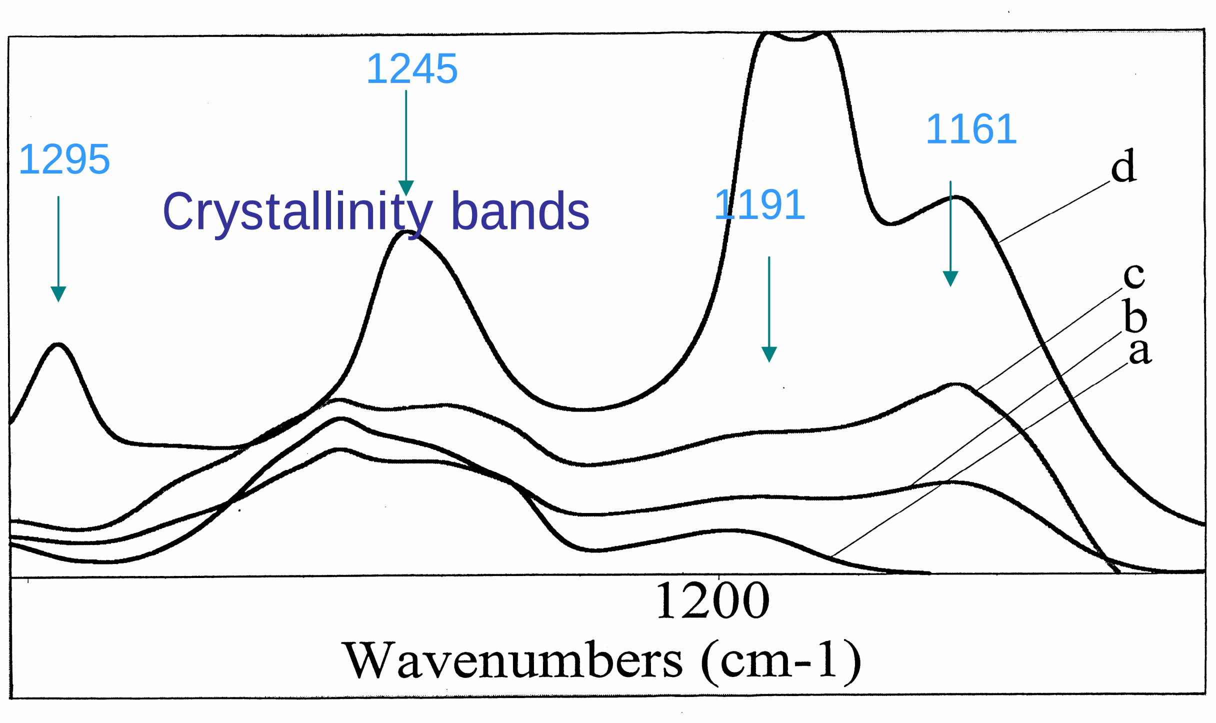
FTIR of 1100-1300 area



Simulated spectra of blends in the zone 1100-1300 cm-1: a) PVC film; b) simulation PCL/PVC, 10%; c) simulation PCL/PVC, 25 %; d) simulation PCL/PVC, 50%; e) PCL film.

results and discussion

FTIR of 1100-1300 area



Spectra of blends in the zone of 1100-1300 cm-1; a) PVC film; b) PCL/PVC, 10%; c) PCL/PVC, 50 %; d) PCL film.

results and discussion

FTIR of 1100-1300 area

In the zone of 1100-1300 cm-1, some bands related to crystallinity, such as 1191,1245 and 1295 cm-1, are detectable. In this zone, the simulated spectra of samples are observed to be different from the real ones. The 1191 cm-1 band, in particular define a decrease - related with the loss of crystallinity - while this decrease does not occur in other bands not related with crystallinity, such as 1166 cm-1. This crystallinity decrease is also seen in the bands 1245 and 1295 cm-1

conclusions

- The spectrophotometric technique enables the characterization of the PCL semycristalline structure at room temperature by means of two differentiated bands for the carbonyl group; interactions between PCL and PVC in the relevant blends can be observed easily.

- Interactions are reflected by the appearance of a new wavelength whose number is between the wavenumber, of the carbonyl group in amorphous state and crystalline state rather than by a continuous displacement of the maximum absorption wavenumber of the blend towards the number of the amorphous state. This means that the carbonyl group in the blend is in a new association state than at existing in PCL pure, and the new association corresponds to the interaction with C-Cl groups of PVC.

conclusions

- Displacements occur not only from the 1721 cm-1 band to higher wavenumber but also from the 1742 cm-1 band to lower wavenumbers.

- The study of the crystallinity in this paper, reveals that the FTIR spectrophotometry technique is capable of detecting the decrease of the PCL crystallinity on increasing the PVC content, the crystallization time remaining constant.

- The comparison of spectra simulated with the real ones is a quick and efficient method to study the blends offering clear results without having to use spectral substractions that can some times be difficult to attain.