Biodegradation Studies of Cellulose and Its Vinylic Graft Copolymers by Thermal Analysis and Mechanical Spectroscopy

C. FLAQUÉ,[1] L. CONTAT RODRIGO,[2] A. RIBES-GREUS[2]

[1] Department of Chemical Engineering, E.T.S.I.I.T., Universidad Politécnica de Cataluña

[2] Department of Applied Thermodynamics, E.T.S.I.I.V., Universidad Politécnica de Valencia, Spain

Received 12 November 1998; accepted 5 June 1999

ABSTRACT: Cotton cellulose with different % NaOH treatments and graft copolymers of cellulose prepared with vinyl acetate (AV) and methyl acrylate (MA), and Ce(IV) ion as an initiator were submitted to biodegradation conditions. Cellulose is a biopolymer consisting solely of glucose units, and, consequently, is also easily biodegradable. Nevertheless, modified cellulose, for example, by graft copolymerization, shows an increased resistance to biodegradation. The aim of this work was to study by calorimetric and dynamic-mechanical analysis how the chemical modification of cellulose affects its biodegradability. From the obtained results some information has also been deduced about the composition and mechanical behavior of the vinylic grafted chains.

Key words: biodegradation; cellulose; graft copolymers; thermal analysis; mechanical spectroscopy

INTRODUCTION

Cellulose is one of the most abundant natural polymer, and has an important role in the development of industrial applications of polymers based on the versatility of properties coupled with their biodegradability and status as a renewable resource. Modification of cotton cellulose by graft copolymerization techniques allows one to chemically change the cellulose chain by introducing polymeric chains that confer different structural characteristics to the initial material. Thus, this allows to develop new cellulosic products with superior mechanical properties to those of conventional celluloses. However, these modifications considerably affect the biodegradation process.[1]

In this article vinylic copolymers of cellulose were prepared by graft polymerization of vinyl acetate (VA) and methyl acrylate (MA) on cotton cellulose initiated by the Ce (IV) ion method.[2] Different cellulosic substrates obtained from purified cotton cellulose treated with NaOH solutions of different concentrations (10 and 20%) were treated with different volumetric ratios of monomers VA/MA (80/20 and 85/15) to achieve different graft percentages (*%G*), which are due to the vinylic chains length and/or to the grafting frequency. The chemical constitution of these macromolecular materials has a significant influence both on the mechanical properties and the biodegradation process because the cellulose hydroxilyc groups have been blocked by the grafted vinylic chains, and this hinders the accessibility of the enzymes produced by the microorganisms of the soil.

When a substance serves as a nutrient for a micro-organism, definitive changes in the chemi-

Correspondence to: M. A. Ribes-Greus.

Journal of Applied Polymer Science, Vol. 76, 326–335 (2000)

cal structure of the material may be produced, caused either by the breakdown of the polymer chain as in the case of pure cellulose, or by the attack only to some chemical bonds as it may occur in the vinylic copolymers of cellulose. Thus, the object of this work was to evaluate the microorganisms attack to the vinylic copolymers of cellulose subjected to a soil burial test, showing that the mechanical and morphological characterization of these copolymers provides measurable quantitative criteria.

EXPERIMENTAL

Materials

The vinylic graft copolymers of cellulose were obtained by the Ce (IV) method as we described in a previous work.[2] For this work we have selected copolymers with two different cellulosic substrates prepared by treatment with a 10% NaOH solution (Cel.B) and a 20% NaOH solution (Cel.D). The volumetric ratios of vinyl acetate and methyl acrylate monomers V_{AV}/V_{AM} were 80/20 and 85/15 called here 1 and 2, respectively. The grafting percentages were determined for all the copolymers (Table I). It is also known that the grafting frequency decreases as CB1 > CD1 > CD2 and the vinylic chain length CD1 > CD2 > CB1.[2] Samples of 2.5 × 1 cm were cut to be submitted to a laboratory soil burial test.

Laboratory Soil Burial Test

A laboratory soil burial test has been carried out according to international standard norms (DIN 53739). The test has been performed in a HERAEUS B6 incubator in which temperature is kept at 28 ± 1°C. Samples have been exposed to microbially active soil over different periods of time: 0, 20, 35, and 84 days. They have been completely buried in a prepared natural soil with a pH (measured in water) of 6.75 and of known maximum water retention capacity (0.804 g H_2O/g humid soil).

Table I Vinylic Copolymers of Cellulose

Copolymer Samples	Cellulose Substrate	% NaOH	V_{VA}/V_{MA}	% Grafting
CD1	Cel.D	20	80/20	305
CD2	Cel.D	20	85/15	184
CB1	Cel.B	10	80/20	136

Table II Degraded and Undegraded T_g Values of Vinylic Copolymers of Cellulose

Exposure Time (Days)	CD1 (305 %G)	CD2 (184 %G)	CB1 (136 %G)
0	27.4	31.5	29.0
35	25.1	27.6	25.1
84	23.0	26.6	23.1

Differential Scanning Calorimetry Measurements

The samples morphology was analysed by Differential Scanning Calorimetry (DSC) with a Perkin-Elmer DSC-4 calorimeter, previously calibrated with indium standard. The sealed pans with about 5–6 mg of sample were scanned at a heating rate of 10°C/min from 0 to 140°C under nitrogen atmosphere.

DSC measurements have been carried out for all the samples before the biodegradation test and after each exposure period (35 and 84 days). In all the cases, the DSC curves show the characteristic peak of the structural relaxation of the material. Because all the samples have been submitted to the same thermal treatment, this peak must be due to the relaxation process that occurs while the samples have been stored before the calorimetric analysis.

The glass transition temperature T_g values have been determined on the DSC curves as described in a previous work.[3] The results are shown in Table II.

Dynamic Mechanical Measurements

The viscoelastic properties were determined by means of a Polymer Laboratories Ltd Dynamic Mechanical Thermal Analyzer, Mark II DMTA. The E' and tan δ values have been measured from −100 to 150°C at the frequencies of 0.3, 1, 3, 10, and 30 Hz, with a heating rate of 1°C/min. The tan δ, E' and E'' values were estimated in N/m^2, with an accuracy of ±0.0001.

The dynamic mechanical measurements of the graft copolymers of cellulose have been performed for the undegraded samples and after 20 and 84 days of exposure. The cellulose sample was already in pieces after 20 days of exposure. For this reason, it was impossible to carry out any dy-

namic mechanical measurement for the degraded cellulose.

RESULTS AND DISCUSSION

To analyze the morphological changes as a function of the degradation time, DSC thermograms were performed for each one of the samples. No glass transition appears for the cellulose in the scan temperature interval. However, its vinylic copolymers present a glass transition near the room temperature, which is attributed to the vinylic PVA-PMA grafted chains. Figure 1 shows the DSC thermograms of copolymer CD2. Similar figures have been obtained for all the copolymers. The T_g values are shown in Table II. These values are lower than the T_g of the PVA alone, which is about 41.8°C, as determined previously,[3] due to the presence of the PMA units in the grafted chains. In this way, copolymers CD1 and CB1 (AV/AM = 80/20) with higher PMA ratio, exhibit lower T_g than copolymer CD2 (AV/AM = 85/15).

On the other hand, it can be observed that the T_g of the degraded samples decreases as the degradation time increases, and therefore, when the cellulose substrate tends to disappear. It can also be noted that the decrease in the T_g when the exposure time increases is greater as the cellulose percentage in the copolymer increases. These facts show that the cellulose hinders the motion of the vinylic grafted chains. It is also observed that

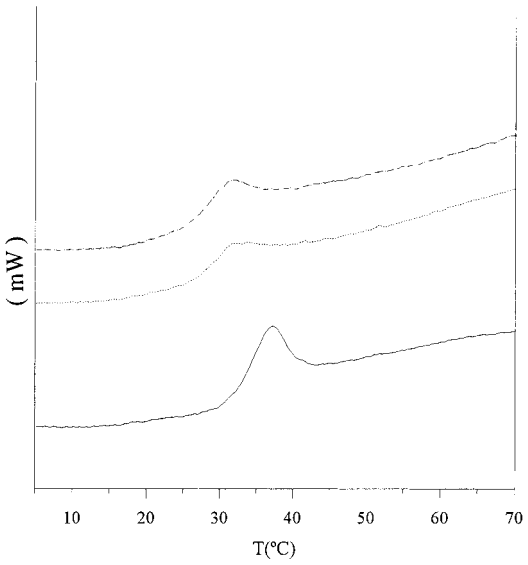

Figure 1 DSC thermograms of copolymer CD2 after different exposure times: —0, · · · 35, and – – –84 days.

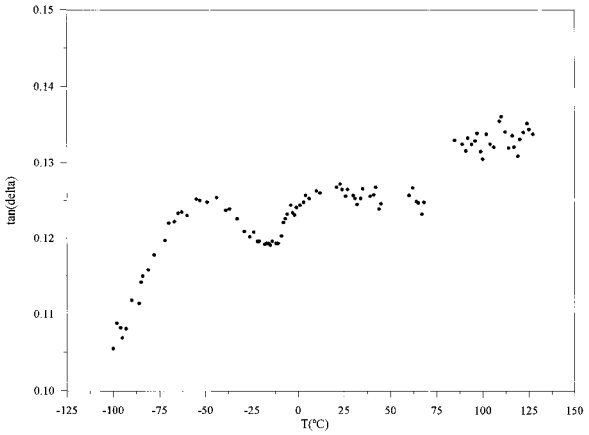

Figure 2 Values of the loss tangent versus temperature at a 10-Hz frequency for undegraded pure cellulose.

the T_g of copolymers CD1 and CB1 has the same value after identical biodegradation times, when the amount of cellulose is decreasing. This can indicate that the PVA/PMA ratio of the vinylic grafted chains is very similar, as it was expected.

The relaxation spectra of cellulose and each one of its vinylic copolymers CD1, CD2, and CB1 have been obtained in terms of the storage modulus (E'), the loss modulus (E'') and the loss tangent (tan δ) as function of temperature.

Figure 2 gives the relaxation spectrum of the undegraded cellulose. Two broad and bad defined peaks around −60 and 10°C have been obtained. The first one has been assigned by other authors[5–7] to motions of OH primary groups in the amorphous region of cellulose. The second peak at 10°C has been ascribed by other authors[3] to the moisture absorbed in cellulose, but its origin is not clear.

Figures 3–4 display the relaxation spectrum of the undegraded vinylic copolymer CD2. Similar figures have been obtained for the other vinylic copolymers, CD1 and CB1. All these copolymers show a well-developed process centered at 40°C, named α, which is attributed to the glass–rubber relaxation of the vinylic side chains,[3,7] because it does not appear in the cellulose.

To characterize this relaxation the experimental data have been fitted to the Fuoss-Kirkwood empirical model:

$$E'' = \frac{E_{\max}}{\cos h\left[m \cdot \frac{E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_m} \right) \right]} \qquad (1)$$

where E_a is the activation energy, R is the gas constant, T_m and f_m are, respectively, the temper-

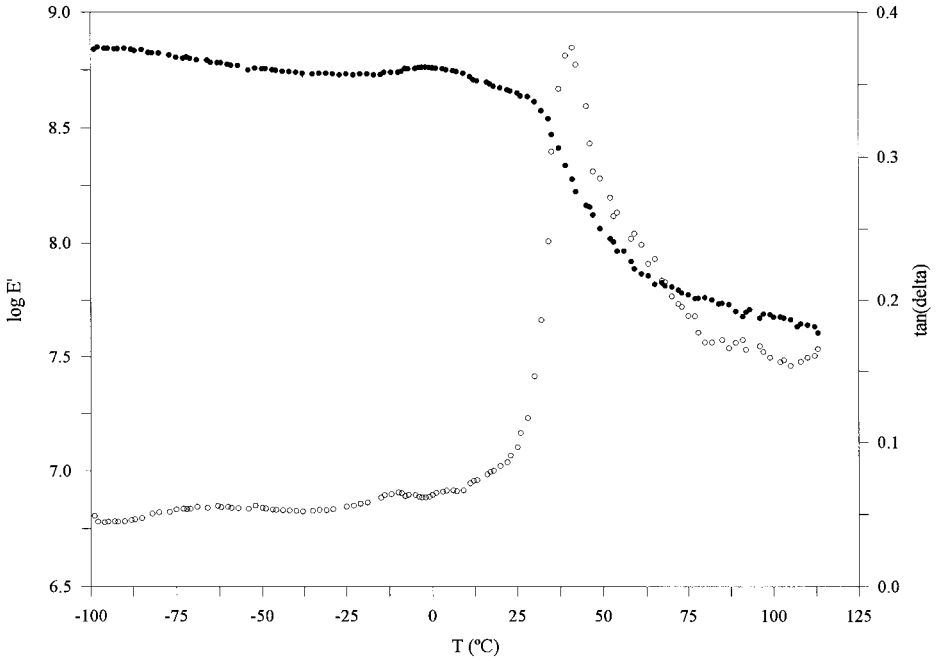

Figure 3 Plot of: ●, log E' and ○, tan δ versus temperature at a 1-Hz frequency for the undegraded copolymer CD2.

ature and the frequency when E'' has a maximum value ($E''_{\max}$) and m is a parameter related to the relaxation width. However, a close inspection of the α-relaxation reveals that the experimental data does not fit adequately to the Fuoss-Kirkwood relationship over the entire range of temperature. This suggests the presence of a small peak overlapped to the α-relaxation, which has

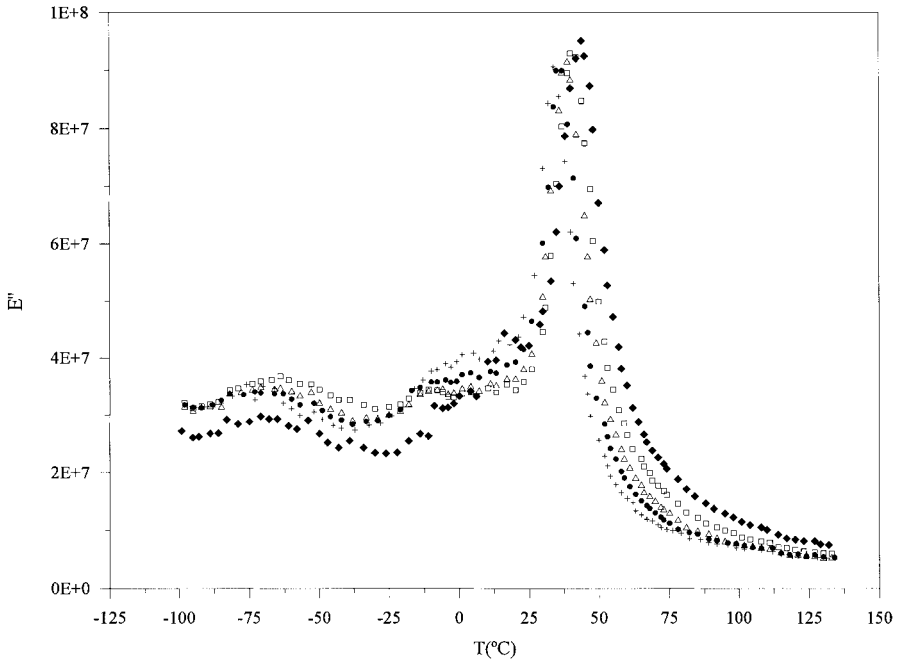

Figure 4 Plot of E'' versus temperature for undegraded copolymer CD2 at different frequencies: ◆, 30 Hz; □, 10 Hz; △, 3 Hz; ●, 1 Hz; and +, 0.3 Hz.

Table III T_m, E''_{max}, and η Values for the α, α', and β Relaxations of the Copolymer CD1 After Different Exposure Periods

		0 Days			20 Days			84 Days		
Relaxation	f (Hz)	log E''_m	η	T_m (K)	log E''_m	η	T_m (K)	log E''_m	η	T_m (K)
α	30	7.86	12,023	313	7.70	12,808	313	8.00	12,374	310
	10	7.85	12,410	310	7.86	14,000	311	7.97	13,194	307
	3	7.85	13,439	308	7.66	14,191	309	7.97	14,387	305
	1	7.85	14,375	306	7.68	15,256	307	7.98	16,852	303
	0.3	7.84	14,687	304	7.67	16,625	305	7.97	17,589	301
α'	30	7.53	2236	264	7.16	4968	263	7.57	3526	289
	10	7.52	2666	269	7.22	3105	267	7.41	2509	268
	3	7.52	2946	271	7.22	3969	266	7.41	2527	265
	1	7.54	3047	271	7.26	5495	266	7.43	2456	264
	0.3	7.56	3381	273	7.27	4887	266	7.46	2861	266
β	30	7.56	1220	231	—	—	—	—	—	—
	10	7.56	1267	228	—	—	—	—	—	—
	3	7.52	1164	226	—	—	—	—	—	—
	1	7.51	1179	224	—	—	—	—	—	—
	0.3	7.50	1317	222	—	—	—	—	—	—

been called α'-relaxation. The experimental data obtained may represent the sum of these two relaxations. Thus, a method employed for the deconvolution of overlapped peaks in dynamic mechanical spectra considers that the measured E'' value is equal to: $E'' = E''_I + E''_{II}$. The T_m E''_{max} and $\eta = m E_\alpha/R$ values for the α-relaxation are shown in Tables III, IV, and V.

The mechanical results are agree with the calorimetric T_g values. As it can be seen in Table III, copolymers CD1 and CB1 show lower T_m values of the α-peak than those of copolymer CD2, confirming the molecular origin of this relaxation. On the other hand, for the same PMA percentage in the grafted chains, the maximum temperature of the α-peak increases with the crystallinity index of

Table IV T_m, E''_{max}, and η Values for the α, α', and β Relaxations of the Copolymer CD2 after Different Exposure Periods

		0 Days			20 Days			84 Days		
Relaxation	f (Hz)	log E''_m	η	T_m (K)	log E''_m	η	T_m (K)	log E''_m	η	T_m (K)
α	30	7.95	10,256	316	6.98	9077	315	7.21	10,173	312
	10	7.95	11,735	314	6.94	9560	313	7.18	10,720	310
	3	7.94	12,183	312	6.93	10,454	311	7.17	11,364	309
	1	7.91	11,284	309	6.94	11,212	308	7.17	12,703	305
	0.3	7.93	13,450	307	6.93	11,509	306	7.16	12,958	303
α'	30	7.59	2338	289	6.73	1214	258	6.80	1844	263
	10	7.54	1846	268	6.67	1728	260	6.73	2125	266
	3	7.55	2134	271	6.66	1637	260	6.74	2434	268
	1	7.58	2233	272	6.67	1752	260	6.74	1428	270
	0.3	7.61	2530	274	6.68	1731	261	6.78	2792	268
β	30	7.47	1024	202	—	—	—	—	—	—
	10	7.56	817	207	—	—	—	—	—	—
	3	7.54	931	204	—	—	—	—	—	—
	1	7.53	869	200	—	—	—	—	—	—
	0.3	7.52	823	197	—	—	—	—	—	—

Table V T_m, E''_{max}, and η Values for the α-, α'-, and β-Relaxations of the Copolymer CB1 after Different Exposure Periods

		0 Days			20 Days			84 Days		
Relaxation	f (Hz)	log E''_m	η	T_m (K)	log E''_m	η	T_m (K)	log E''_m	η	T_m (K)
α	30	8.42	13,505	314	7.75	13,974	313	7.83	13,553	307
	10	8.38	11,881	312	7.75	14,777	310	7.83	15,144	305
	3	8.35	12,727	310	7.74	16,242	309	7.81	15,373	302
	1	8.34	12,897	308	7.74	17,690	307	7.83	17,644	300
	0.3	8.33	13,539	306	7.73	18,198	304	7.82	18,575	298
α'	30	7.95	1132	243	7.26	3605	263	7.34	2856	263
	10	7.90	1492	258	7.29	4157	264	7.37	3321	265
	3	7.92	1900	266	7.29	3862	264	7.37	3251	263
	1	7.93	2000	268	7.31	3416	263	7.40	3331	264
	0.3	7.94	2172	268	7.32	3246	263	7.42	3451	263
β	30	8.07	968	207	—	—	—	—	—	—
	10	7.99	915	212	—	—	—	—	—	—
	3	7.95	892	210	—	—	—	—	—	—
	1	7.94	773	204	—	—	—	—	—	—
	0.3	7.92	778	200	—	—	—	—	—	—

the cellulosic substrate (crystallinity index: Cel.D = 0.48 and Cel.B = 0.58).[4] This suggest again that the cellulose main chain hinders the motion of the vinylic grafted chains. When the crystallinity index of the cellulosic substrate increases, the difficulty of the vinylic motions increases. It may be interesting to examine more closely the effect of all these factors on the apparent activation energy of the α-relaxation.

Figure 5 shows the Arrhenius diagram where the α- and α'-relaxations are represented. Assuming that the α-relaxation is related to the glass transition, and to study the dependence of the mean relaxation times with the temperature the experimental data have been fitted to the Vogel equation:[8]

$$\ln f_m = A + \frac{B}{T_m - T_\infty} \tag{2}$$

where T_m and f_m are, respectively, the temperature and the frequency when E'' has a maximum value (E''_{max}). A, B, and T_∞ are three parameters that result from the application of a least-squares fit to an experimental ln f_m versus $1/T_m$ values set. Dielectric results obtained from other works[4–6] for the dielectric α-relaxation have been considered to carry out the determination of these parameters.

The T_∞ parameter is the temperature that would correspond to a zero free volume, and is

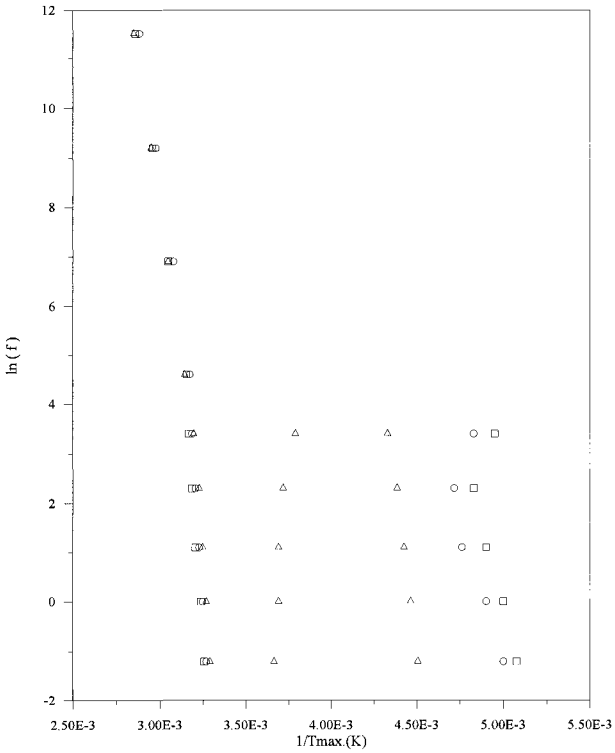

Figure 5 Arrhenius map for the undegraded copolymers of cellulose showing: the α-, α'-, and β-relaxations for sample CD1 (△) and the α- and β-relaxations for samples CD2 (□), and CB1 (○). Dielectric results obtained from other works[4–6] for the dielectric α-relaxation have been considered as CD1 (△), CD2 (□), and CB1 (○).

Table VI Parameters of the Vogel Equation for the α-Relaxation of the Undegraded and Degraded Vinyl Copolymers

Exposure Time (days)	T_∞	B	E_a (300 K) (kcal/mol)
CD1 Copolymer			
0	250.4	1387	100.7
20	248.1	2125	141.0
84	246	1832	112.3
CD2 Copolymer			
0	254.5	1461	126.2
20	250.6	1769	129.6
84	249.6	1595	112.3
CB1 Copolymer			
0	252.0	1583	122.8
20	248.1	838	55.6
84	246.1	686	42.2

generally related to the glass transition temperature as follows: $T_\infty = T_g - 50$.

According to the Doolittle equation,[9] B is related to the free volume ϕ:

$$B = [(h/\phi)/(T - T_\infty)] = [(h/\phi_g)/(T_g - T_\infty)] \quad (3)$$

where ϕ and ϕ_g are the free volumes at T and T_g, respectively, and h is a constant whose value is near unity. In the Vogel model, the apparent activation energy depends on the temperature, and is related to the B and T_∞ parameters by the following relationship:

$$E_a = R \cdot B \cdot \left(\frac{T}{T - T_\infty}\right)^2 \quad (4)$$

Table VI shows the Vogel parameters and the apparent activation energy for the α-relaxation of the undegraded vinylic copolymers of cellulose. The obtained apparent activation energy is higher for the CB1(136%G) and CD2 (184%) copolymers whose cellulosic substrate has a higher crystallinity index, its vinylic chains are shorter, and its grafting frequency lowest, as our previous results.[2] Between CD1 (305%G) and CD2 (184%G) copolymers with the same cellulosic substrate, the CD1copolymer, with a higher PMA/PVA ratio and longer vinylic chains than CD2, shows lower activation than CD2. These results may indicate that the intramolecular interaction seems to become more significant when cellulosic substrate is more crystalline and when the length of the vinylic chain and its PMA/PVA ratio makes easier the chain motions.

On the other hand, the characteriszation of the α′-relaxation is difficult because it is smaller than the α one. The E''_{max}, T_m, and η Fuoss-Kirkwood parameters were also calculated, but the values are less significant. Calorimetric results suggest the possibility to attribute it to a structural relaxation.

Another subglass-relaxation, labeled β, can be observed in the relaxation spectrum. This relaxation is broader than the α one. The maximum temperature of the β-peak at 1 Hz of frequency is −49, −69, and −73°C for copolymers CD1, CB1, and CD2, respectively. These values suggest that the localization of this relaxation in the temperature axis is sensitive to the cellulose ratio in the copolymer and to the crystallinity index. But it seems unrelated to the composition of PVA/PMA vinylic side chains, because copolymers CD1 and CB1 must have the same ratio, and show a very different maximum temperature. This result may suggest that this relaxation may be due to the β-relaxation of cellulose. It is generally assumed that this relaxation is related to movements of —OH primary groups in the amorphous region of cellulose.[5–7]

To analyze these mechanical relaxations, the experimental data have been fitted to the Fuoss-Kirwood model. The obtained values are shown in Tables III, IV, and V.

The activation energies for this relaxation have been calculated according to the Arrhenius equation:

$$\ln f = \ln f_0 + \exp\left(\frac{E_a}{RT}\right) \quad (5)$$

The calculated apparent activation energies are 53, 27, and 22 kcal/mol for copolymers CD1, CD2, and CB1, respectively. However, these values are higher than those reported by other authors for the β-relaxation of pure cellulose, which are about 12 kcal/mol. However, the biodegradation process may contribute with more information.

Figures 6–7 show the dynamic mechanical results of the degraded vinylic copolymers of cellulose. The differences observed in the relaxation spectrum of the degraded samples also agree with the calorimetric results.

The α-relaxation shifts to low temperatures when the exposure degradation time increases

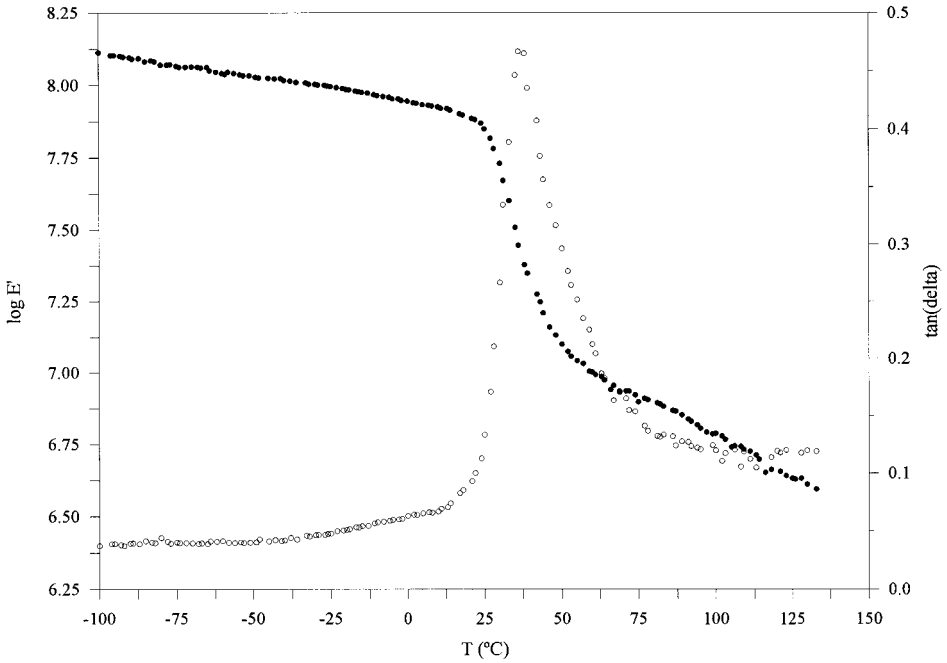

Figure 6 Plot of: ●, log E' and ○, tan δ versus temperature at a 1-Hz frequency for copolymer CD2 after an exposure time of 84 days.

and the micro-organisms attack the cellulose chains. The decrease in T_m is greater for CB1, which, besides to have the higher percent cellulosic substrate, is more crystalline, as it can be seen in Tables III, IV, and V, and in Figure 8. The decrease in the temperature of the α-peak, when the exposure time increases, displays the following sequence: CB1 > CD2 > CD1.

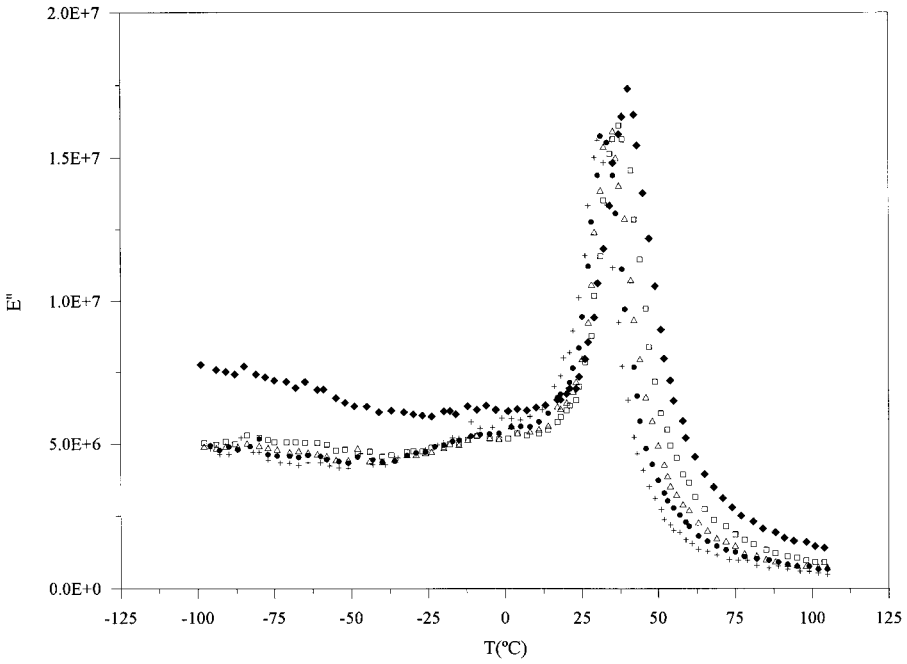

Figure 7 Plot of E'' versus temperature for copolymer CD2 degraded 84 days at different frequencies: ◆, 30 Hz; □, 10 Hz; △, 3 Hz; ●, 1 Hz; and +, 0.3 Hz.

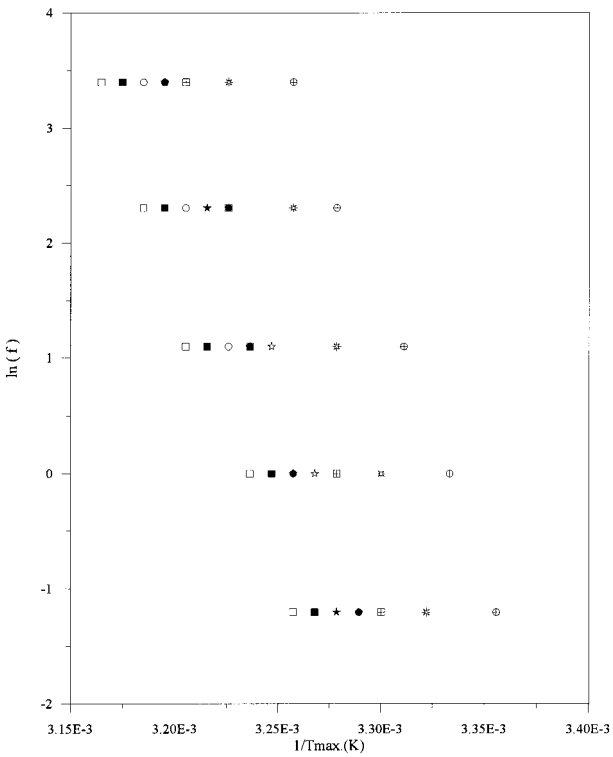

Figure 8 Arrhenius map of the α-relaxation of the cellulose copolymers: ☆, undegraded CD1; ★, CD1 degraded 20 days; *, CD1 degraded 84 days; □ undegraded CD2; ■, CD2 degraded 20 days; ⊞, CD2 degraded 84 days; ○, undegraded CB1; ●, CB1 degraded 20 days; and ⊕, CB1 degraded 84 days.

Thus, the biodegradation of these vinylic copolymers of cellulose must be related with the number of the —OH groups of cellulose blocked by both the hydrogen bonds in the crystalline regions and by the grafting. At the same time these results agree with the biodegradation mechanism proposed by other authors,[10] and with the idea that there is a strong link between degree of substitution and biodegradability.

On the other hand, Table VI shows the apparent activation energy values, estimated from eq. (4), obtained from biodegraded copolymers CD1, CD2, and CB1.The estimated apparent activation energy decreases fast in the CB1 when the biodegraded time increases, while CD2 and CD1 show an unregular evolution. These results suggested that the apparent activation energy is sensitive to the cellulose substrate, and the intramolecular interaction decreases as the glucose units are attacked by the micro-organism. This attack is quicker when the grafting frequency is lower.

The small peak (α'-relaxation) overlapped to the α-relaxation remains the same.

Because the α-relaxation disappears when the biological attack has been produced, and the vinylic chains have not been affected, the molecular origin of this relaxation has been associated to movements of molecular groups (primary —OH) in the cellulose chain. The vinylic chains block the —OH groups of cellulose and hinder their motion. Thus, the apparent activation energy increases when the grafting percentage increases. At the same time these results agree with the biodegradation mechanism proposed by other authors.[10] Accessible —OH groups are needed in the main chain, and there should be several unsubstituted glucose molecules in the cellulose chain before the biodegradation attack can begin.

CONCLUSIONS

The α-relaxation of graft copolymers of cellulose is due to the glass transition of the vinylic chains. However, the cellulosic backbone hinders the motion of the vinylic-grafted chains. The intramolecular interaction is more significant in a more crystalline cellulose substrate, with a lower grafting frequency and a lower chain length.

The β-relaxation of graft copolymers of cellulose is related to movements of the —OH primary groups in the amorphous region of cellulose. However, the vinylic chains block the —OH groups of cellulose and hinder their motion. Thus, the apparent activation energy increases when the grafting percentage increases.

The introduction of vinylic grafts onto the cellulose chain hinders the biodegradation process. Through the analysis of the mechanical behavior of the polymers as well as their morphological changes, it is possible to study the biodegradation effects on the vinylic-grafted copolymers of cellulose.

The biodegradation process as it is shown is related with the free —OH groups of cellulosic substrate, and therefore, with the degree of mercerization of cellulose its crystallinity index and with the grafting percentage related to the conditions of the mercerized cellulose cotton. The biodegradation increases when the number of —OH groups of cellulose blocked by the grafting decreases. As the grafting percentage is lowered,

the cellulose copolymers became more biodegradable. Thus, copolymer CB1 is more biodegradable than copolymers CD1 and CD2.

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