Effects of Moisture and Degradation Time over the Mechanical Dynamical Performance of Starch-Based Biomaterials

JOÃO F. MANO, RUI L. REIS, ANTÓNIO M. CUNHA

Department of Polymer Engineering, University of Minho, Campus de Azurém, 4800 Guimarães, Portugal

ABSTRACT: The viscoelastic behavior of a polymeric system composed from a blend of starch and a copolymer of poly(ethylene-vinyl alcohol)-(SEVA-C)- was studied by dynamic mechanical analysis. Two main relaxation processes, at about 30 and 90°C, were identified, and their kinetic behavior was studied. The studied materials are being considered for a range of orthopedic applications, which demands the characterization of the dependence of its solid rheological properties upon moisture content. Additionally, it is of main importance to study the evolution of its dynamic mechanical properties as a function of immersion time in simulated physiological solutions. A plasticization effect due to moisture was clearly observed on the low-temperature relaxation. The degradation of SEVA-C in 0.154 M NaCl and 0.154 M NaCl+10% v/v bovine serum solutions provided indication that no significant decreasing of stiffness is observed for times up to 60 days. The effects of an enzymatic environment were evident, the degradation processes being much faster in the later solution. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2345–2357, 2000

Key words: thermoplastic starch; biomaterials; viscoelastic behavior; DMA; mechanical properties

INTRODUCTION

There is a need for the development of novel degradable polymeric biomaterials exhibiting an adequate balance of mechanical properties and degradation kinetics. However, most of the biodegradable polymers being used in clinical practice do not exhibit an undoubtedly biocompatible behavior, and their mechanical properties are usually not enough to allow for their utilization on load demanding applications. Several studies[1–8] have been proposing alternative systems, based on corn starch incorporating blends, for a range of biomedical applications including bone replace-

ment/fixation, filling of bone defects, tissue engineering scaffolds, *in situ* polymerazible bone cements, hydrogels, and drug delivery carriers.

It has been shown that blends of starch with poly(ethylene-vinyl alcohol) or cellulose acetate may present a biodegradable behavior as well as an interesting mechanical performance.[1–7] The incorporation of bone-like inorganic fillers, such as hydroxyapatite (HA), allows for the development of bioactive degradable composites with an interesting range of mechanical properties.[4,6,7] It was also reported that the physical properties of those materials can be further optimized by controlling the morphologic developments within the molds by using nonconventional processing routes.[4–7] Biodegradable systems under consideration for being used on tissue replacement/fixation, or as tissue engineering scaffolds to be ap-

plied in load-bearing sites, must exhibit mechanical properties that match those of human bone, associated to a degradation kinetics adequate to the healing of the tissues to be replaced or fixed. Furthermore, it is of main importance to realize that these systems will have to withstand cyclic loading when implanted, and to try to characterise their viscoelastic response under such types of conditions. Nevertheless, the mechanical characterization of novel biomaterials when subjected to dynamic loading is usually scarce.

The demands required for biomedical application of degradable polymeric-based systems require a careful and extensive study of their properties at different levels, including among others: biocompatibility (*in vitro* and *in vivo*), degradation behavior, surface chemistry, and an extensive mechanical characterization. Related to this later area, the investigation of the viscoelastic properties of such materials may be of great interest, because one can not only simulate the physiological dynamical loading, but can also access relevant fundamental information at the molecular level, both from a structural and dynamic perspective. The dynamic mechanical analysis technique (DMA) is a very suitable tool for investigate the viscoelastic properties of polymers in a wide range of temperatures and frequencies.[9,10] In fact, this technique has also been used on polymeric biomaterials (e.g., refs. 11–15, and references therein).

In a previous study we have used DMA to characterize the effects of the amounts of hydroxyapatite fillers and introduction of porosity over the viscoelastic properties of starch-based blends.[16] DMA proved to be a very powerful research tool to obtain a deeper understanding of the mechanical behavior of these very complex blends, and it was possible to correlate results with those obtained on quasi-static mechanical testing. In this work, DMA was used to investigate the effects of the moisture content and of the degradation level caused by simulated physiological solutions on the materials' mechanical response. In fact, it is of main importance to understand the effects of water uptake over the properties of water-sensitive polymers, and to follow its degradation behavior from a mechanical point of view, trying to obtain information about the respective relevant molecular changes/adjustments. This is even more important for this type of complex systems, as their degradation cannot be followed by molecular weight measurements being just inferred from rheological tests. However, to date, the degrada-

tion of these novel biomaterials has just been studied, as a function of time, based on weight loss, water uptake, and evolution of the quasi-static mechanical properties.[3–4,7] Although some complementary characterization techniques have been used, no information on structural and viscoelastic changes at the molecular level is available on the literature. Furthermore, the combined effects of moisture and cyclic loading over the materials mechanical performance have not, to our knowledge, been reported.

EXPERIMENTAL

Materials and Materials Preparation

The studied material was a blend of starch and a copolymer of poly(ethylene-vinylalcohol) (composition of the copolymer: 60/40 mol/mol), referred as SEVA-C, supplied by Novamont, Novara, Italy with a melt flow index (MFI) value of 0.71 g/10 min (170°C, 49 N). Another blend, corn starch/cellulose acetate (SCA), also from Novamont, Novara, Italy was used to facilitate the assignment of the processes related to the starch fraction from those attributed to ethylene-vinyl alcohol (EVOH). Both blends are commercially available, and their composition is not made known; however, previous tests indicated that the weigh volume fraction of starch is about 50% in both blends. Moreover, SEVA-C is a complex interpenetrated network, while SCA is a nonmiscible blend.

Further details on the production and characteristics of the study materials may be found in works by Bastioli et al.[17–19] Also, an extensive characterization of these materials that focuses on their potential for biomaterials uses has been recently published.[1]

A Klockner-Ferromatik Desma FM20 conventional injection-molding machine was used to produce small ASTM dumb-bell tensile test samples (cross-section 2×4 mm^2). The processing conditions were optimized so as to maximize the mechanical performance of the molded parts, as described in the references.[5,6]

Three humid SEVA-C samples were obtained by keeping three virgin samples within a cavity on a wet piece of cotton during different periods of time ($t_1 \approx 50$ min $t_2 \approx 100$ min, and $t_3 \approx 150$ min). The direct contact between the samples and the cotton was minimized to avoid any unwanted degradation of the materials. The moisture factor for each humid samples ($h_1 = 0.41\%$ $h_2 = 1.51\%$, and

$h_3 = 2.61\%$) has calculated as the increase of weight of the samples relatively to their initial weight. A "dry sample" was obtained by drying a virgin sample in a excicator for 3 days. A loss of 0.51% of the samples initial weight was observed.

Two solutions were used for the investigation of the degradability of SEVA-C blends. A very simple, 0.154 M NaCl (referred hereafter as NaCl solution) isotonic saline solution was selected to simulate the body extracellular fluids. In some tests a bovine serum (BS), Sigma C-6278, St. Louis, MO, was added to the 0.154 M NaCl solution in a concentration of 10% v/v, to evaluate the effects of proteins over the materials degradation (referred hereafter as NaCl+BS solution). The samples were immersed in the solution during different times (1, 3, 4, 7, 14, 30, and 60 days). The measurements were always carried out after allowing the moisture content of the degraded samples to stabilize for 2 weeks in a room with a controlled atmosphere (23°C, 55% RH).

Experimental Methods

The DMA measurements were carried out using a DMA7e Perkin-Elmer apparatus with a controlled cooling accessory, in the temperature range from −15 to +130°C. High-purity helium was used for purging the sample environment during the experiments.

The three-point bending experimental method was used in all the experiments: the samples were placed over a 15-mm bending platform, and a 5-mm knife-edge probe tip provided the mechanical excitation: in all experiments a static stress of 1.20 MPa and a dynamic stress of 1.00 MPa were imposed to the sample. Those stress values were sufficiently small to assure that the strain is within the linear viscoelastic range.

All experiments were carried out during heating at 4°C/min. The temperature calibration at the same heating rate was done following the procedure described in ref. 20, using an Indium standard. Several frequencies were used between 0.5 and 20 Hz. At each temperature scan 500 points were collected. For some cases, the comparison are made only at 1 Hz.

When using the DMA technique it is usual to measure the temperature dependence of the dynamic modulus ($E^* = E' + iE''$) and loss factor (tan $\delta = E''/E'$) during heating while the sample is vibrated at a particular frequency. While the storage modulus is related to the elastic stiffness of the material, the loss modulus reveals the viscous components of the material being related to the energy absorbed by the sample during its dynamic excitation.

Quasi-static tensile tests were also performed, in a controlled environment (23°C and 55% RH) using an Instron 4505 universal mechanical test machine fitted with a resistive extensometer (gauge length, 10 mm). The molded specimens were previously conditioned at 23°C and 55% HR for 2 weeks. The stiffness of the several samples was characterized by means of the secant modulus of 1% strain ($E_{1\%}$). This characterization was carried out only for the samples degraded in the simulated physiological solutions. The idea was to compare, in a qualitative way, the storage modulus obtained under a flexure dynamic solicitation with that of standard quasi-static tensile data. Both tests probe the elastic stiffness of the materials, although the obtained results are not usually the same (see, e.g., ref. 16).

RESULTS AND DISCUSSION

Virgin SEVA-C

The DMA results of the virgin material are shown in Figure 1(a)–(c). In the temperature range of −20–120°C, two main processes may be observed, both being clear on the loss and storage moduli plots. The low-temperature process is located at ≈30°C (maximum of E'' at 26°C for $f = 1$ Hz), and the high-temperature one at ≈90°C (maximum of tan δ at 96°C for $f = 1$ Hz). Note that no transitions were found by DSC at these temperature regions, indicating that no appreciable changes in C_p are associated to those relaxations.[1] To be able to attribute these two processes to any specific relaxation mechanisms, it was decided to compare the DMA spectrum of SEVA-C with that of SCA. The storage modulus and the loss factor of an SCA sample (stabilized moisture content as described in the Experimental section) are presented on Figure 2. All experimental conditions were identical to those selected for SEVA-C samples. The attribution of the higher temperature relaxation to a mechanism that is occurring within the starch fraction was supported by the fact that a relaxation was also found in the same temperature region for SCA. On this material, the synthetic component of the blend has been changed (cellulose acetate instead of EVOH), but
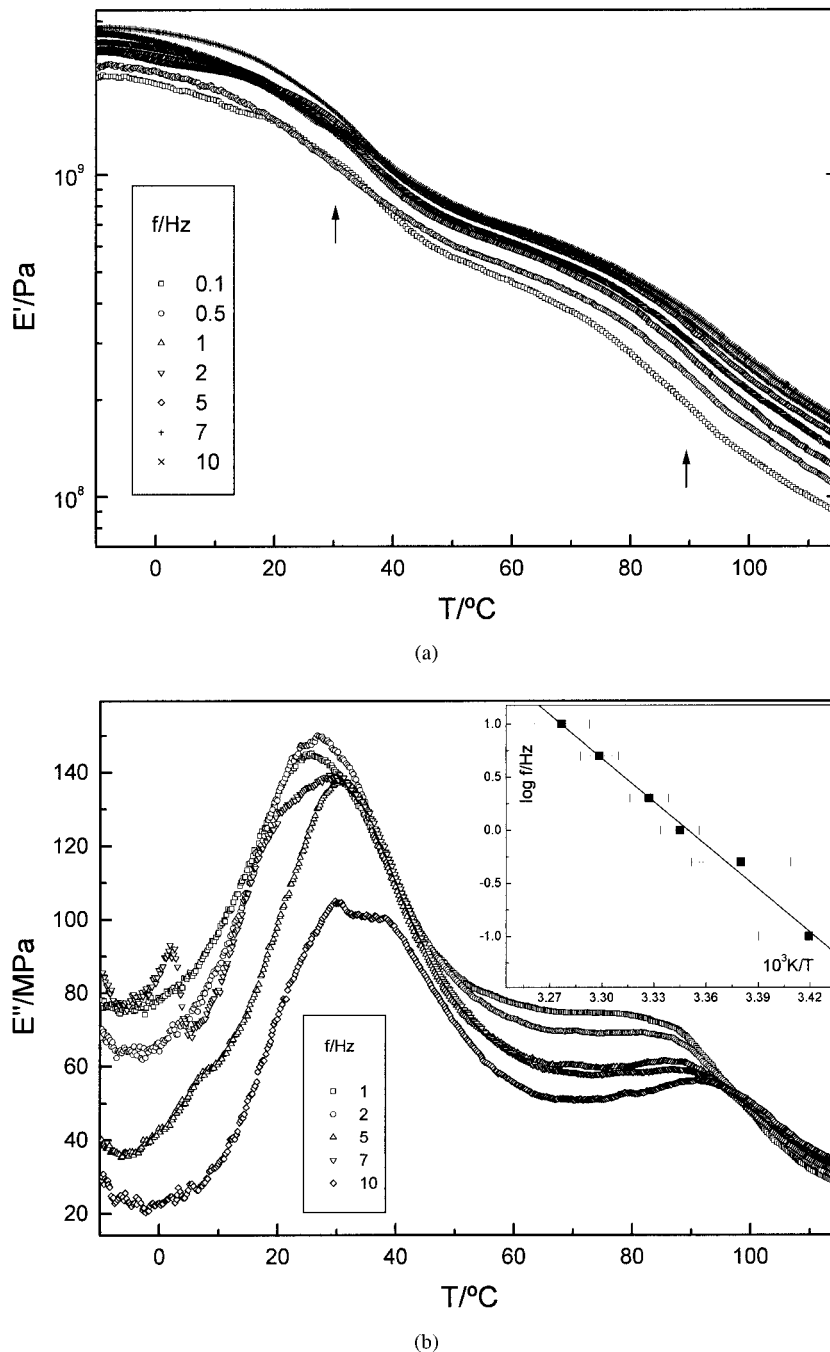
(a)

(b)

Figure 1 (a) Frequency dependence on the storage modulus for virgin SEVA-C material. The arrows indicate the temperature region of the two main processes [see (b) and (c)]. (b) Frequency dependence on the loss modulus for virgin SEVA-C. The inset graphics show the corresponding Arrhenius plot for the $\approx 30°C$ process and the respective linear fitting. (c) Frequency dependence on the loss factor for virgin SEVA-C. The inset graphics show the corresponding Arrhenius plot for the $\approx 90°C$ process. The dot line corresponds to the fitting with the VFT equation and the solid line corresponds to the Arrhenius fitting.

the starch fraction was maintained. In a similar line of thinking, the absence of a 30°C peak in Figure 2 seems to indicate that the lower temper-

ature relaxation on SEVA-C should be related to the EVOH component or to a complex between EVOH and amylopectin.
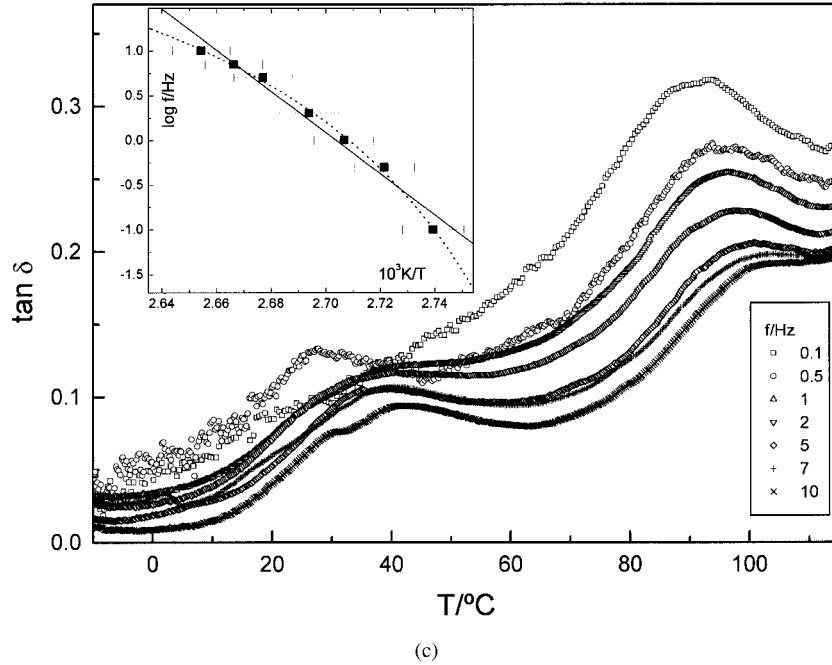
(c)

Figure 1 (*Continued from the previous page*)

SCA was only studied with the purpose of assigning with a higher confidence level the peaks present on SEVA-C. In fact, the aim of the present work was to study the behavior of SEVA-C, as it will be clear from the remaining part of the text.

The dependence of the viscoelastic parameters of SEVA-C shown in Figure 1(a)–(c) with frequency allows us to obtain further information about the dynamics of the different mechanisms. As expected, from Figure 1(a), the material stiff-

ens with increasing frequency, and the different processes shift to higher temperatures. The stiffening of the material with increasing frequency is shown in Table I as the value of E' at 80°C for the different frequencies. At lower temperatures, the scatter of the results is much more intense, making difficult this appreciation.

It can be noticed that at 23°C the storage modulus, for the range of frequencies studied, has a value of about 1.5 ± 0.5 GPa. This value may be
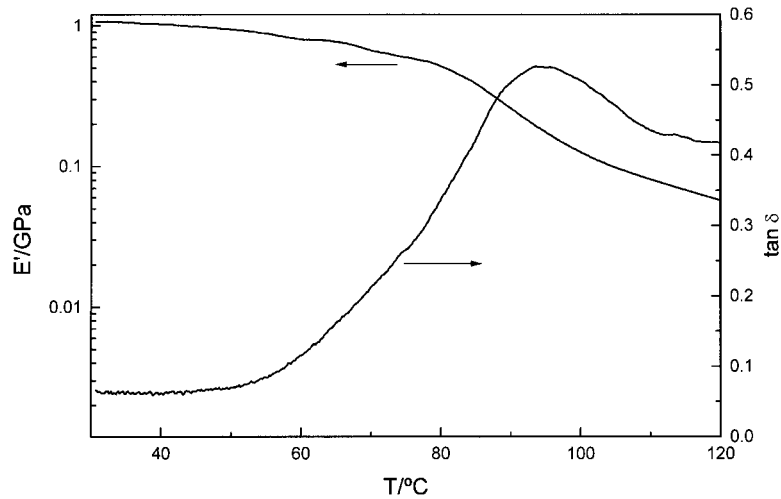

Figure 2 Storage modulus and loss factor for SCA obtained at 1 Hz.

Table I   Storage Modulus at 80°C, Temperature of Maximum E'' for the Low-Temperature Relaxation and Temperature Maximum of Tan δ for the Higher Temperature Relaxation of Virgin SEVA-C at Different Frequencies

f/Hz	E'(80°C)/GPa	T(max E'')/°C Relaxation at ~30°C	T(max tan δ)/°C Relaxation at ~90°C
0.1	0.28	19	92
0.5	0.34	23	94
1	0.39	26	96
2	0.41	27	98
5	0.45	30	101
7	0.47	31	102
10	0.48	32	104

roughly compared with the tensile modulus that has been reported to be in the 1.9 ± 0.5 GPa range.[1–5]

By comparing Figure 1(b) and (c), it can be conclude that the relaxation at 30 °C is clearly seen in the loss modulus graphics, as an intense peak. On the other hand, the higher temperature relaxation appears in the loss modulus plot as a shoulder in the curves and is much well visible in the tan plot as a very broad peak in the temperature axis.

The relaxation map of the process at ≈30°C (log f vs. 1000/T, where f is the frequency and T is the temperature of maximum loss modulus, also presented in Table I) is shown in the inset of Figure 1(b). Considering that in this case the temperature dependence of the relaxation times follows an Arrhenius dependence (log f = log f_0 − E_a/[ln(10)RT], where f_0 is a preexponential factor, and R is the constant gas), the linear regression of the data gives an activation energy of E_a = 260 kJ · mol^{-1}. This value is relatively low for a conventional glass transition, but is sufficiently high to eliminate a hypothesis of any secondary process. These results are also an indication that the involved molecular motions have clearly a cooperative nature. Consequently, one may conclude that the low temperature relaxation should be related to the diffusion motion of the large molecular segments of the copolymer. It should also be mentioned that the temperature dependence of the relaxation/retardation times of the glass transition relaxation are usually fitted with a Voguel-Fulcher-Tammann (VFT) equation: f = f' exp[−A/(T−T_0)]. An extended discussion of this point can be found elsewhere.[21] The absence of any curvature in the Arrhenius plot in Figure 1(b) may be eventually caused by the narrow frequency range used in the experiments.

The temperature location and the nature of the low temperature relaxation may be extremely relevant for the application purposes of SEVA-C. In fact, Figure 1(b) shows that this process presents a broad and intense peak in the loss modulus spectra throughout the room temperature and human body temperature, for a dynamical stresses of about 1 Hz. On the other hand, it is known that E'' is a measure of the dissipation of mechanical energy imposed, with a specific frequency, to the sample. This means that the cyclic mechanical solicitation with time scales of the order of 1 s can be dissipated by means of internal friction between the molecular entities responsible for the relaxation observed at ≈30°C. As suggested before, those can be relatively large segments of the copolymer fraction.

As commented before, the loss peak of the relaxation at ≈90°C is weak, but the corresponding tan δ peak is much more intense. This means that this higher temperature process has the capability to dissipate a large amount of mechanical energy relatively to the energy stored in an elastic form. Therefore, the dynamics of the process at ≈90°C is studied, in this case from the observation of the frequency dependence upon the temperature location of the tan δ peaks [Fig. 1(c)]. The temperature of maximum tan δ for each studied frequency is also presented in Table I. The Arrhenius plot, shown in the inset of Figure 1(c), suggests a VFT behavior, typical for relaxation processes involving cooperative motions of the molecular species. The dot line corresponds to an nonlinear fitting according to the VFT equation. It must be noticed that the temperature axis used in this case corresponds to the temperature of maximum loss factor. Therefore, the obtained adjustable parameters will not be discussed because the data to be used came from the E'' (or D'', the
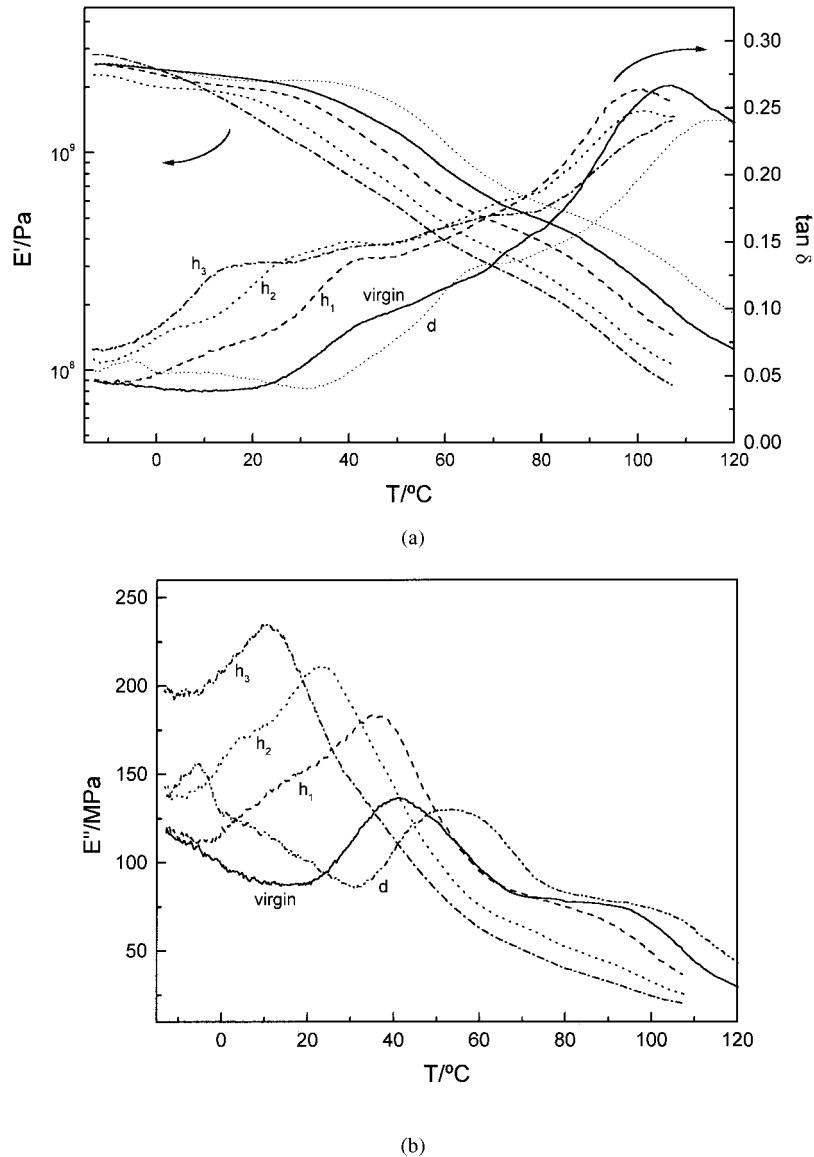
(a)

(b)

Figure 3 (a) Storage modulus and loss factor for different water contents in SEVA-C. The solid lines are for the virgin material. The h_1, h_2, and h_3 lines are for increasing water contents (h_1 = 0.41% h_2 = 1.51%, and h_3 = 2.61% of weigh increase) and the d line is for the dry sample (d = 0.51% of weigh loss). The experiments were carried out at 1 Hz. (b) Temperature dependence of the loss modulus for the same materials shown in (a).

loss compliance) results. However, to be compared with the 30°C relaxation, a rough value of the activation energy of the higher temperature relaxation, obtained by fitting the results with the Arrhenius equation [solid line in the inset graphics of Fig. 1(c)] gave 440 kJ · mol^{-1}. This value indicates that the molecular motions involved in the high-temperature process are more hindered than in the lower temperature process.

Effect of Moisture

The humid samples, prepared as explained in the Experimental section, and the dry sample were immediately tested after weighing. The humid samples showed an increase of weigh of, respectively, h_1 = 0.41% h_2 = 1.51% and h_3 = 2.61%, and the dry sample presented a weigh loss of d = 0.51%. All experiments were carried out at 1
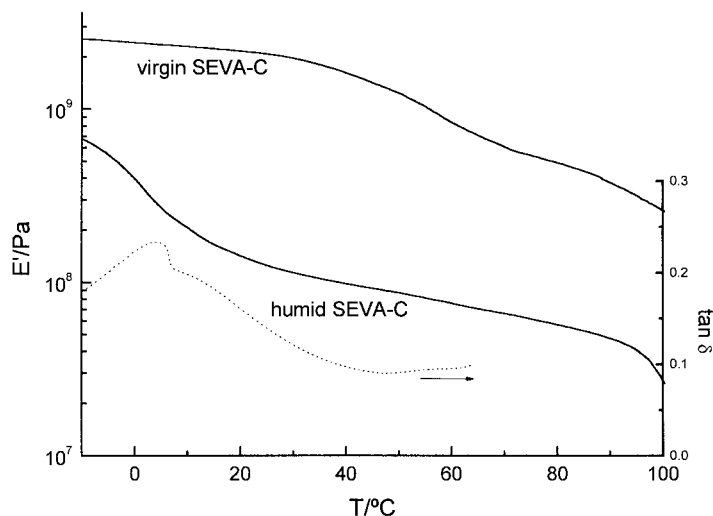
Figure 4   Solid lines: storage modulus at $f = 1$ Hz for the virgin SEVA-C and for a very humid SEVA-C sample. The dotted curve corresponds to the tan δ for the humid sample.

Hz. The viscoelastic spectrum of the humid samples, a nontreated sample (equilibrium moisture content at 23°C and 55% RH), and the dry sample, are shown as a function of temperature in Figure 3(a). A systematic effect of moisture over the mechanical behavior of the material is quite visable. The characterization of this dependence is, of course, of main importance for systems being assessed for potential use as biomaterials. The storage modulus decreases with the water uptake in the studied temperature range. However, a higher value of E' at temperatures around 0°C for the higher water content sample can be observed, which may be caused by the stiffening effect of the ice.

The moisture also effects the mobility at the molecular level. It can be seen, from the tan δ curves, that the process at 30°C shifts to lower temperatures with increasing water content. This effect can be ascribed to the plasticization effect of water on the cooperative motions of the segmental chains involved in this process. Moreover, this effect also enhances the intensity of molecular motion processes within this temperature region, leading to an increase of the relaxation strength with increasing water content. Both effect are also very well visible in the E'' vs. T curves, shown in Figure 3(b).

The presence of water molecules in SEVA-C seems to have a different influence over the process at 90°C. As explained before, this relaxation may be assigned to molecular motions within the starch fraction. Those molecules may undergo, to some extent, a modest hydrolysis process, weakening this relaxation (see tan δ and E'' plots). This process can progressively induce the appearance of low molecular mass material, which may explain the shoulder of the tan δ curves at $\approx$70°C, which shifts to lower temperatures with increasing water content. Another possible explanation is to attribute these observations to the plasticization by water of the more amorphous areas of the starch-containing fractions that will lead to a structural lubrication effect. This correlates well with the shift of tan δ peak to higher temperatures observed for the dry sample (the temperature of maximum tan δ is 107 and 116°C for the virgin and dry samples, respectively). As other phenomena such as retrodegradation may be involved, further research is required to unambiguously explain the effects of moisture around the 90°C relaxation.

Experimental implications may also influence the results such as the variation of water content in the sample. In fact, we must be aware that the initial moisture level is not maintained during the DMA experiment, where the temperature is slowly increased. Complementary tests performed at the same experimental conditions allowed observation of significant variations on the water content relatively to the initial value (decreasing of $\sim$15 and $\sim$78%, respectively, at 35 and 85°C). This evidence clearly shows the need for future tests under environmental controlled conditions. Presently we are in the process of developing equipment that will allow performance
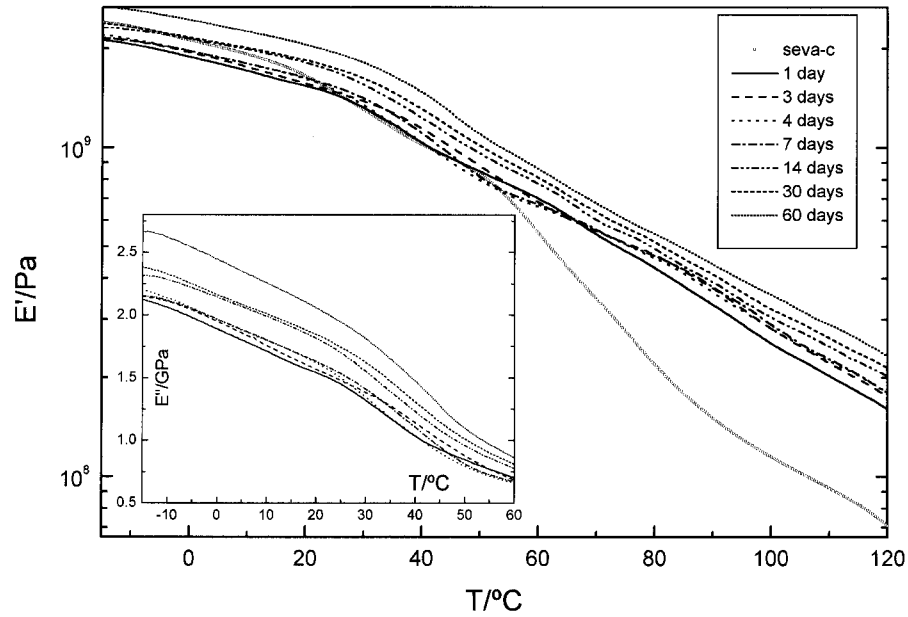
(a)
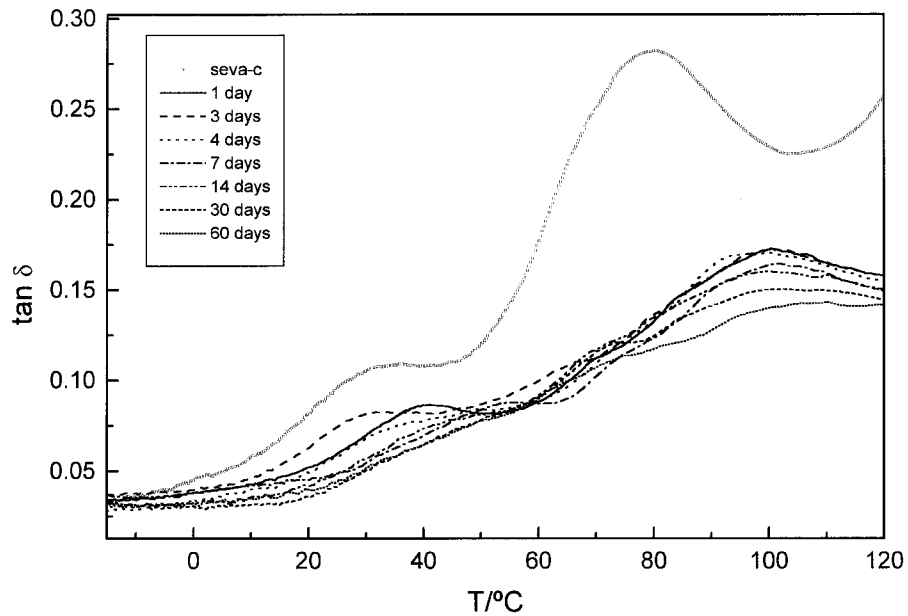
(b)

Figure 5 (a) Degradation of SEVA-C in NaCl solutions in the storage modulus at f = 1 Hz for different immersed times. The inset graphics presents the curves up to 60°C in a linear scale. (b) Degradation of SEVA-C in NaCl solutions in the loss factor modulus at f = 1 Hz for different immersed times.

tests on immersed samples in simulated physiological solutions. A good example of this kind of apparatus is found in ref. 11, where the water evaporation is controlled over a significant temperature range.

As explained before, the humid samples (h_1, h_2, and h_3) had water contents up to +2.61%. To test

the SEVA-C material exposed to an extremely humid ambient, DMA experiments were also carried out with a sample previously immersed in distilled water for 3 days (water uptake of 22.5% by weight). From Figure 4 it can be concluded that this process leads to a decrease of the storage modulus of about one order of magnitude. This

Table II   Storage Modulus at 37°C and 1 Hz for the SEVA-C Samples Degraded in NaCl and NaCl + BS Solutions

Degradation Time/Days	$E'(37°C)/GPa$ Samples in NaCl Solution	$E'(37°C)/GPa$ Samples in NaCl + BS Solution
1	1.12	1.34
3	1.22	1.23
4	1.13	1.32
7	1.20	1.30
14	1.32	1.33
30	1.41	1.45
60	1.59	1.39

means that these polymers are very sensitive to water, and that their properties will be deeply affected in saturated humidity conditions. Results for hydroxyapatite reinforced SEVA-C and starch-based samples processed by Scorim[4,6] are much more encouraging, and the water uptake is deeply reduced. This fact leads to a much less significant decrease in the mechanical properties, which can be as low as 30% (when comparing samples conditioned to equilibrium water content and to a saturated moisture situation content). Furthermore, unpublished data show that it is possible to crosslink these systems, overcoming this type of problem. A peak in the tan δ curve observed at ≈5°C can probably be explained by the fusion of ice. No other process was observed in this plot up to 65°C (above this temperature the material was too soft to extract any reliable value of the loss factor).

Degradation in Simulated Physiological Fluids

The aim of the DMA studies on materials previously immersed in simulated physiological solutions is to follow the material degradation process by changes in its viscoelastic behavior. In fact, most protocols used to study the degradation of biodegradable polymeric biomaterials are based on following the evolution of weight loss, water uptake, and changes in static mechanical properties as a function of time. DMA is a ready-to-use technique that might provide for additional information on the degradation type dependence upon the solid rheological behavior of this type of material. Furthermore, the obtained DMA data may allow for the prediction of the mechanical performance of these novel materials when cycle loaded in a physiological environment.

As pointed out before, in this particular work two solutions were used: an isotonic saline solution 0.154 M NaCl (NaCl), and NaCl +10% v/v bovine serum (NaCl+BS). The latter was aimed at studying the influence of an enzymatic media over the material's degradation.

The evolution of the storage modulus and tan δ with the immersion time in the NaCl solution is shown in Figure 5(a) and (b). In Figure 5(a), a progressive difference in stiffness between the virgin sample and all the degraded specimens for testing temperatures above ≈50°C can be observed. This is clear even for the shorter immersion time (1 day). The results for the different immersion times present a small evolution in the studied temperature range. However, a careful examination shows that the storage modulus increases with increasing immersion time. (The values of E' at 37°C for the different degradation times is shown in Table II.) This behavior at lower temperatures is clearly seen in a linear E' scale [see inset in Fig. 5(a)]. This stiffening effect may be explained by the previously reported loss of platicizer that occurs in the first degradation stages of the studied starch-based blends.[3,4] A model to describe the degradation behavior of starch-based polymeric and composite biomaterials has recently been proposed.[22] It was shown that initially there is a structural lubrication by water, followed by a loss of plasticizer and other processing aids, and only for longer times (depending on sample geometry) chemical degradation with backbone scission, associated with a clear decrease of stiffness. In this study, the latter process was not found after 60 days of immersion time, as observed not only on DMA measurements but also on quasi-static tensile tests (see
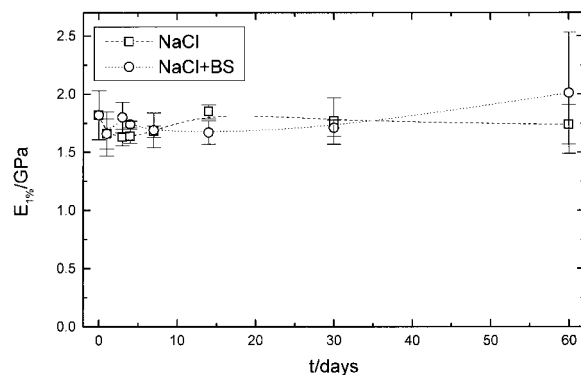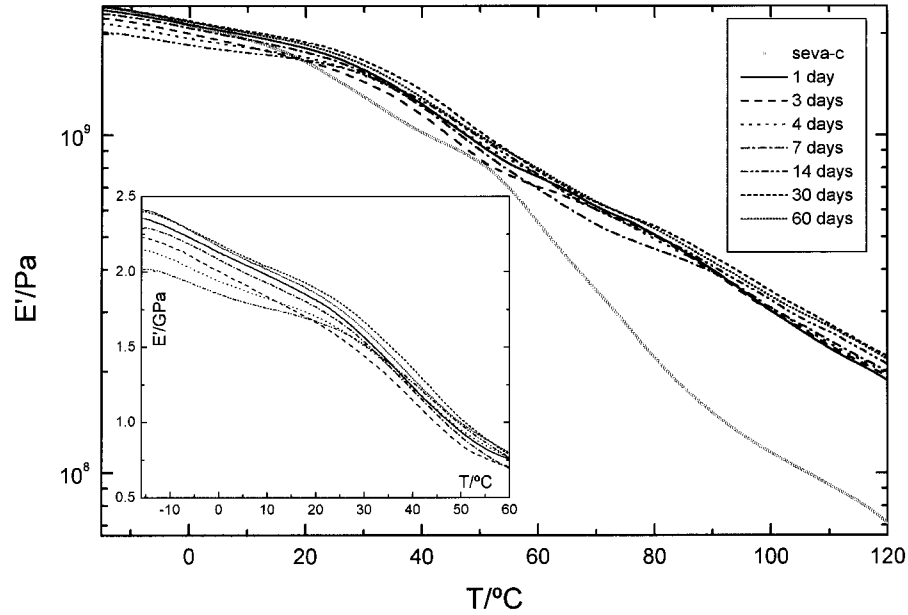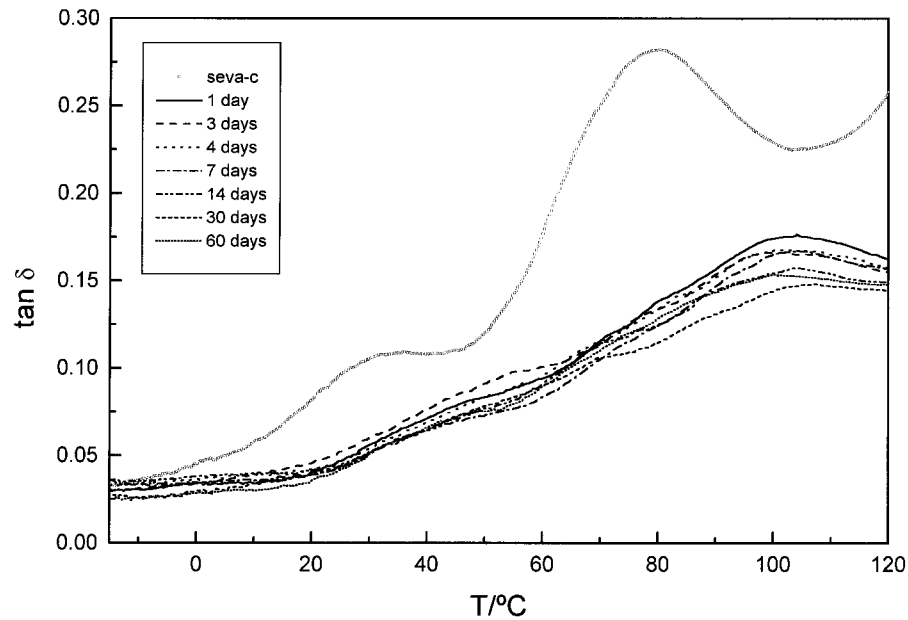

Figure 6   Quasi-static modulus at $f = 1$ Hz of SEVA-C after immersion at different times in NaCl (squares) and NaCl+BS (circles) solutions.

(a)

(b)

Figure 7 (a) Degradation of SEVA-C in NaCl+BS solutions as seen by the evolution of the storage modulus at $f = 1$ Hz for different immersion times. The inset graphics presents the curves up to 60°C in a linear scale. (b) Degradation of SEVA-C in NaCl+BS solutions as seen by the evolution of the loss factor at $f = 1$ Hz for different immersion times.

Fig. 6). This behavior might be desirable for structural applications such as bone plates and screws on which a mechanical behavior similar to that of human bone is required in the first few months after implantation; at longer times, chemical deg-radation should lead to the resorption of the implant, avoiding a second surgery for its removal. The herein reported results must be obtained in the future for much longer times to get a complete picture of the material's degradation behavior.

Nevertheless, it is worth mentioning that for non-coupled hydroxyapatite-reinforced composites a much faster decrease of mechanical stiffness has been observed in previous studies due to a preferential attack at the polymer–ceramic interface.[4]

The degradation behavior in the NaCl solution can also be seen in a tan δ plot, as shown in Figure 5(b). This allows for distinguishing the degradation mechanisms throughout the different relaxation processes. The figure points out that the degradation process leads to less intense peaks, shifted to higher temperatures (an exception was found between 1 and 3 days). This can once again be explained by the total loss of plasticizer that hinders the macromolecular mobility.

It is interesting to see that, relative to the virgin material, the relaxation at ≈90°C undergoes a more drastic change than the relaxation at 30°C. This seems to indicate that the modifications during degradation take place preferentially on the starch-containing fraction of the blends. One may speculate that there is a selective attack to the more amorphous regions of this fraction due to their higher water uptake ability, which tends to attenuate the tan δ peaks as time goes by. This results on leaching of some broken low molecular weigh chains to the degradation media.

Similarly, Figure 7(a) and (b) shows the degradation effect occurring in the NaCl+BS solution. As in the previous case, there is a clear change from the virgin to all the degraded materials above 50°C. The more important observation is that degradation occurs faster in this medium than in the NaCl solution. This is particularly clear when comparing Figures 5(a) and 7(a) and Figures 5(b) and 7(b). In fact, the variation of the curves corresponding to the samples immersed in NaCl+BS solution for degradation times above 1 day is much more attenuated then with the degradation in NaCl solution. The values of E' at 37°C for the degradation in NaCl+BS solution are shown in Table II, and can be compared with the evolution of these values with the degradation in NaCl solution. This behavior can be explained by the enzymatic effect of the BS component, which accelerates the degradation process of the SEVA-C material, namely the platicizer extraction.[22]

CONCLUSIONS

The dynamic mechanical behavior of SEVA-C, a blend of starch and a copolymer of poly(ethylene-vinyl alcohol) presented two main relaxation processes in the temperature range of -15 to 130°C. The relaxation at 30°C, with an activation energy of 260 kJ · mol^{-1}, was assigned to segmental mobility of the copolymer or to its complex with amylopectin, whereas the relaxation at 90°C, with an activation energy of 440 kJ · mol^{-1}, was attributed to molecular motions within the more linear starch fraction.

The effect of moisture on the viscoelastic properties of SEVA-C show a decrease of the storage modulus, and a clear plasticization effect was observed in the relaxation at 30°C.

The degradation of SEVA-C in NaCl and NaCl +bovine serum solutions provided indication that no significant decreasing of stiffness is observed for times up to 60 days. The effects of an enzymatic environment were evident, the degradation processes being much faster in the later solution.

The dynamic mechanical performances of SEVA-C material associated with its degradation behavior might allow for its use on demanding biomedical applications that must withstand loads. However, to be able to apply these materials on load-bearing implants, further research is needed to develop formulations that are less sensitive to moisture. This can be achieved by several routes, including using nonconventional injection-molding technologies (morphological control), reinforcing the blends with stiff bone-like ceramics and/or developing ways of crosslinking the blends.

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