Thermal Stability of Polycaprolactone/Nafion Blends Prepared in the Presence of 3-Aminopropyltriethoxysilane

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ABSTRACT: Polycaprolactone (PCL) and Nafion blends were prepared in the presence of 3-aminopropyltriethoxysilane (3-APTEOS) by a sol–gel reaction. The presence of 3-APTEOS allowed the preparation of macroscopically homogeneous self-supported films of PCL/Nafion blends in a wider composition range. The thermal properties of the blends were evaluated by thermogravimetric analysis and differential scanning calorimetry. The thermal stability of the blends decreased as the Nafion content increased. The reduction of the thermal stability of PCL in the presence of Nafion was confirmed with Fourier transform infrared/photoacoustic spectroscopy, and it was attributed to the possible hydrolysis of PCL caused by the reaction with the SO_3H acid groups of Nafion. An opposite effect on the thermal stability of the blends was caused by the addition of 3-APTEOS. The increase in the thermal stability of the blends with the increase in the 3-APTEOS content was assigned to the neutralization of the acid groups of Nafion by the formation of an ionic complex. The differential scanning calorimetry results showed that PCL and Nafion were immiscible. The degree of crystallinity of PCL slightly increased with an increase in the Nafion content, whereas the melting temperature remained basically unchanged. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3701–3709, 2004

Key words: blends; thermal properties

INTRODUCTION

Mixing different polymers is one of the most important ways of obtaining materials with specific properties. The principal aim in blending polymers is attaining a synergistic effect in the final material, which should have better properties than each individual component. In practice, this is very difficult to achieve because most polymer pairs are thermodynamically immiscible, and this results in fragile materials with macroscopic phase segregation and poor adhesion between the different phases. To improve the interfacial adhesion and to reduce the domain size, an interfacial agent, generally a compatibilizer, must be used in polymer blends.[1]

In this work, we wanted to obtain a material that had properties such as flexibility, biocompatibility, biodegradability, and ionic conductivity and the potential to be used in bone and tissue implants. One of the selected materials for this purpose was polycaprolactone (PCL), a flexible, biocompatible, and biodegradable polyester, which has been extensively used in medical devices and bone implants.[2–5] Another polymer used in our work was Nafion, which is a biodegradable and biocompatible ionomer and ionic conductor. Nafion contains a poly(tetrafluoroethylene) backbone and sulfonic acid end groups.[6] In biological applications, Nafion has been commonly used for the protection of biosensors.[7–10]

PCL/Nafion blends are completely immiscible and show macroscopic phase segregation; therefore, it is necessary to use an interfacial agent. In this work, 3-aminopropyl triethoxysilane was used to achieve a finer dispersion of the polymeric phases because it forms biocompatible hybrids with PCL[11–13] and Nafion.[10] The silicon alkoxide forms a silicon oxide based three-dimensional network containing —Si—OH and —NH_2 by a sol–gel process. The Si—OH end group can react with organic polymer groups, such as the hydroxyl and carboxyl groups of PCL, by polycondensation, and this results in the formation of an inorganic–organic hybrid nanocomposite .[11] However, the amine end groups can interact with the acid groups of Nafion.

In this work, PCL/Nafion blends containing different 3-aminopropyltriethoxysilane (3-APTEOS) and Nafion concentrations were prepared by a sol–gel reaction and were characterized by solubility testing, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The effects of the Nafion and 3-APTEOS contents on the thermal stability of PCL were evaluated with TGA, DSC, and Fourier transform infrared/photoacoustic spectroscopy (PAS–FTIR).

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EXPERIMENTAL

Materials

Nafion (equivalent weight = 1100) in a 5 wt % solution in an aliphatic alcohol with about 20 wt % water, PCL (weight-average molecular weight = 80,000 g/mol), and 3-APTEOS were purchased from Aldrich (São Paulo, Brazil) and used as received.

Preparation of the hybrids and blends

In this work, PCL/3-APTEOS and Nafion/3-APTEOS are called hybrids, whereas PCL/Nafion/3-APTEOS mixtures are called blends.

PCL hybrids, Nafion hybrids, and blends were prepared as follows. 3-APTEOS was partially hydrolyzed with 1:3 (mol/mol) 3-APTEOS/water in previously distilled tetrahydrofuran (THF). This solution was stirred for 30 min, and then the polymer solution was added to prehydrolyzed silicon alkoxide: (1) PCL in a 5 wt % solution in THF or a similar Nafion solution for hybrid preparation and (2) both polymer solutions, PCL and Nafion, for blend preparation. The resulting solutions were then stirred for 3 h and transferred to 5-cm-diameter Teflon dishes. Glass dishes were avoided because of the adhesion of alkoxysilane to glass. The covered dishes were kept inside a desiccator for 24 h to allow the reaction to occur and to prevent solvent evaporation. After this, the solvent was allowed to evaporate in a desiccator saturated with a solvent vapor, and this resulted in films 0.1–0.3 cm thick. These films were dried at room temperature for 24 h and were further dried *in vacuo* at 25°C for 8 h.

The PCL content in the blends was varied from 50 to 90 wt %, and the 3-APTEOS content was 0, 1, 2.5, 5, or 10 wt % with respect to the total polymer weight. The concentration of 3-APTEOS used in the PCL hybrids was the same as that used in the blends. Only the Nafion hybrid containing 10 wt % 3-APTEOS was prepared.

Solubility testing

About 0.05 g of the blends and the PCL or Nafion hybrids was dispersed in THF under stirring for 3 h at 25°C to verify the solubility.

Thermal analysis

The thermal stabilities of the blends and hybrids were evaluated in a Netzsch TG 209 thermal analyzer (Selb, Germany). Samples (~10 mg) were heated at 10°C/min from 25 to 800°C under a nitrogen atmosphere.

DSC was obtained with an MDSC 2910 thermal analyzer from TA Instruments (New Castle, DE). Samples (~10 mg) were heated at 20°C/min from −140 to 100°C in the first heating and from −140 to 300°C in the second heating under an argon atmosphere. The cooling scan from 100 to −140°C was performed at 20°C/min. Indium was used for calibration, and the glass-transition temperature was obtained from the half-height of the slope change of the heat capacity plot. The results of the second heating are used in the discussion. The heat flow was normalized with respect to the sample mass.

The repeatability limit for TGA and DSC was 1°C because the experimental conditions, such as the heating rate, purge gas flow rate, and sample weight, were kept constant.

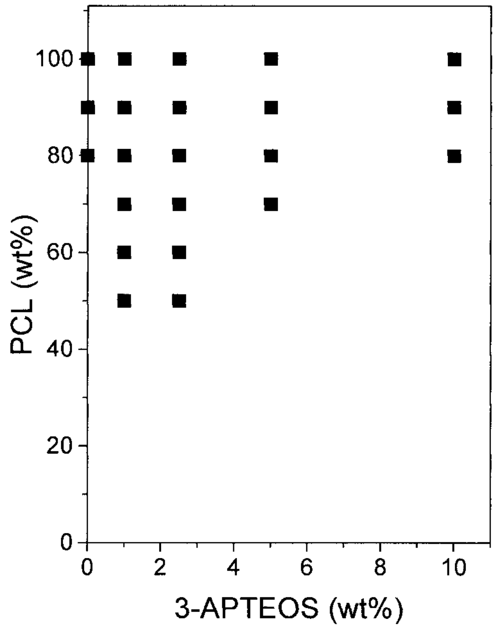


Figure 1 Compositions of the self-supported films of the hybrids and blends.

PAS–FTIR

PAS–FTIR analyses were performed with a Bomem MB series B100 spectrometer (Quebec, Canada) equipped with a photoacoustic accessory. All spectra were recorded from 400 to 4000 cm^{-1} at 25°C at a resolution of 8 cm^{-1} with 256 scans. The photoacoustic cell was purged with helium gas.

This analysis was performed for PCL, Nafion, and a PCL/Nafion (80/20) blend, before and after the thermal treatment. The thermal treatment was conducted in an Edgcon SP alumina tubular oven (São Carlos, Brazil) under an argon atmosphere at 10°C/min from 25 to 245°C, and the blend was kept at 245°C for 1 h. The samples were analyzed as solid films, except for the thermally treated PCL/Nafion (80/20) blend, which was analyzed in a powder form.

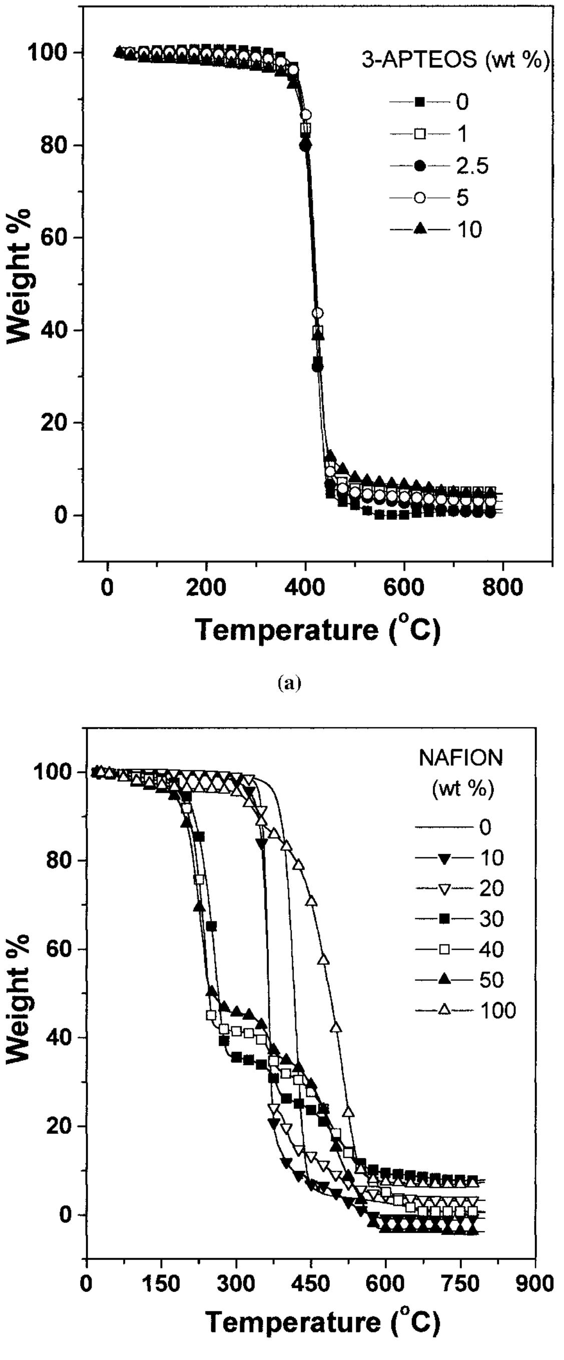


Figure 2 Thermogravimetric curves for (a) PCL hybrids and (b) PCL/Nafion blends containing 2.5 wt % 3-APTEOS and different Nafion contents.

RESULTS AND DISCUSSION

Sample physical characteristics

The PCL hybrid films, as well as the pure PCL films, were white, flexible, and homogeneous in all the composition ranges studied. The Nafion film was brown and flexible.

A mixture of PCL and Nafion resulted in films that showed macroscopic phase segregation with poor adhesion between the phases. This behavior is typical of immiscible and incompatible blends. To promote a finer and homogeneous distribution of the phases, 3-APTEOS was added to the blends at low concentrations (up to 10 wt %). Blends richer in PCL, obtained with 3-APTEOS, were flexible and macroscopically homogeneous, and their color depended on the Nafion content. White films were obtained with up to 20 wt % Nafion. Blends containing 30–50 wt % Nafion were slightly brown. The flexibility of the blends decreased as the Nafion content increased. The preparation of self-supported films of blends was possible with very well defined Nafion and 3-APTEOS contents, as shown in Figure 1.

The blends in which the Nafion content was higher than 20 wt % presented considerable shrinkage during solvent evaporation.

The Nafion hybrid containing 10 wt % 3-APTEOS was very brittle, and it was not possible to obtain a self-supported film.

Solubility testing

The aim of this test was to evaluate the solubility of the blends and the polymer hybrids to demonstrate the influence of 3-APTEOS on the formation of clusters in Nafion. THF was used because it is a good solvent for PCL. All the PCL hybrids were completely

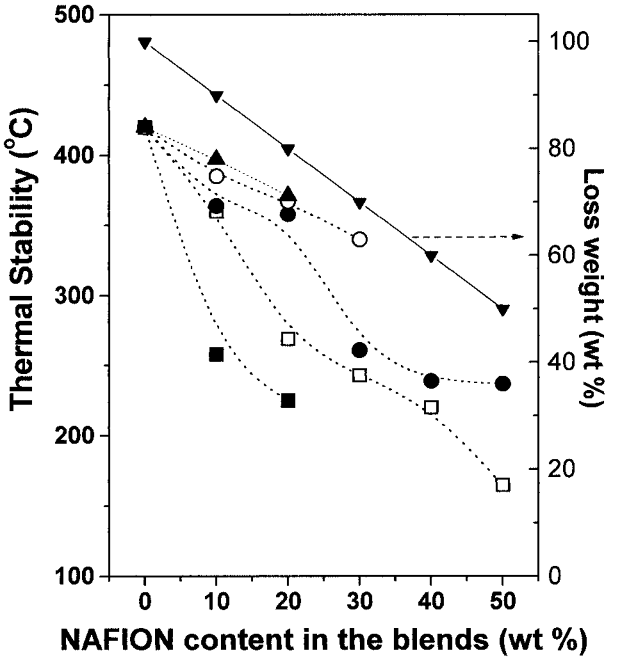


Figure 3 Thermal stability temperature for PCL/Nafion blends containing different 3-APTEOS concentrations (wt %) as a function of the Nafion content: (■) 0, (□) 1, (●) 2.5, (○) 5, and (▲) 10 wt %. (▲) The weight-loss percentage was observed for blends containing different Nafion concentrations.

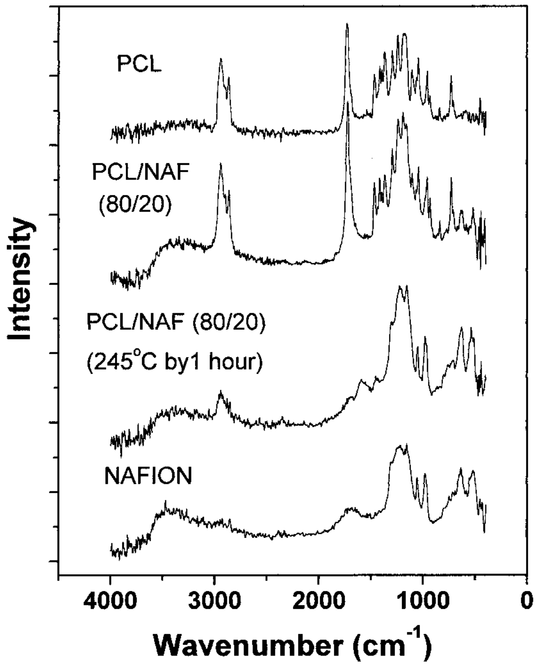


Figure 4 PAS–FTIR for PCL, Nafion, and a PCL/Nafion (80/20) blend.

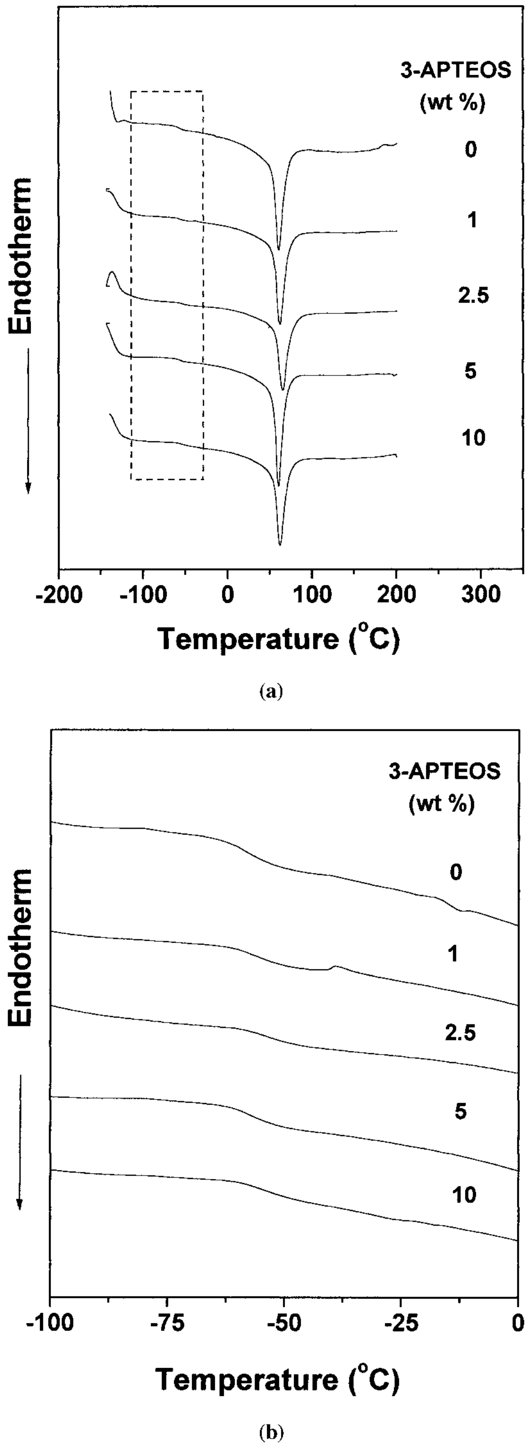
soluble in THF, and no gel fraction was observed. This fact suggests that PCL should be bonded in the silica network mainly by hydrogen bonding, as observed by Tian et al.[14] in a study of PCL and tetraethoxysilane (TEOS) hybrids.

THF causes swelling of Nafion film but, at 25°C, cannot dissolve it. The solubility of Nafion film is possible only under high-pressure conditions because this ionomer undergoes decomposition at high temperatures. The morphology of Nafion is described in the literature[15,16] as consisting of polar clusters in a hydrophobic matrix. These clusters are formed by pendent ionic groups on the Nafion backbone and act as physical crosslinking, conferring high solvent stability. The Nafion hybrid containing 10 wt % 3-APTEOS was completely soluble in THF at 25°C, with no gel fraction, and this indicated that the introduction of 3-APTEOS should hinder the formation of these polar clusters during film casting. Tamaki and Chujo[17] studied the interactions in hybrids of poly(styrenesulfonic acid) and 3-APTEOS by ^{1}H-NMR; their results indicated the formation of a quaternary salt, —$NH_4^+SO_3^-$. Similar ionic interactions should occur between Nafion and 3-APTEOS groups, which can be explained by the hypothesis of the formation of a quaternary salt between the —SO_3H Nafion groups and the —NH_2 group of 3-APTEOS. This fact was probably responsible for the better Nafion dispersion in the blends containing alkoxysilane. All blends containing 3-APTEOS were also soluble in THF, whereas blends without alkoxysilane resulted in a fine dispersion of Nafion in THF.

Thermal analysis

TGA

The thermal stability of the homopolymers, blends, and PCL hybrids was evaluated by TGA. In thermogravimetry, the thermal stability of a material is associated with the initial temperature at which mass vari-



(a)

(b)

Figure 5 DSC curves for PCL hybrids: (a) full temperature range and (b) glass-transition-temperature range.

TABLE I
DSC Results for PCL Hybrids: Glass-Transition Temperature (T_g), Melting Temperature (T_m), Enthalpy of Melting (ΔH_m), and Corrected Degree of Crystallinity (x_c)

3-APTEOS (%)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_{mc} (J/g of PCL)	x_c[a]
0	−60	60	61	61	41
1	−59	62	57	58	39
2,5	−59	65	54	55	37
5	−59	60	59	62	42
10	−58	62	55	61	41

[a] Calculated with the heat of fusion for pure PCL crystals as 148 kJ/mol.[24]

ation is observed. TGA thermograms for PCL hybrids are shown in Figure 2(a). Only one weight-loss stage was observed for pure PCL, which occurred at 420°C, and the temperature of this thermal process was not shifted by the addition of 3-APTEOS. PCL hybrids lost about 1.5 wt % at approximately 100°C. This weight loss must be associated with the condensation reactions of ethoxysilane or residual silane groups, resulting in organic volatiles and water. PCL hybrids also presented residues at 800°C due to the formation of silica.

The thermogravimetric curves for the pure homopolymers and their blends containing different Nafion contents and 2.5 wt % 3-APTEOS are shown in Figure 2(b). The first weight-loss process for Nafion was observed from 75 to 200°C and was attributed to residual water loss.[18] Two other processes could also be observed: the first one occurred at 340°C, and the main process occurred at 520°C. Deng et al.[19] identified the evolution of SO_2, due to the degradation of SO_3^- groups, and of CO_2 up to 400°C by the TGA–FTIR technique. These authors also observed the release of HF up to 450°C associated with the decomposition of the side chains and backbone of Nafion.[19]

The thermal decomposition profile of the blends was dependent on the Nafion and 3-APTEOS contents. All the blends showed a mass loss around 100°C due to residual water and further condensation of silanol groups. This process is not taken into account in this discussion of the thermal stability of the blends; only the processes occurring at higher temperatures are considered. The increase in the Nafion concentration in the blends caused a drop in the thermal stability with respect to the pure homopolymers, as shown in Figure 3. The addition of only 10 wt % Nafion caused a drop of 160°C in the thermal stability of the PCL/Nafion blend without 3-APTEOS, with respect to pure PCL. The weight loss in this process corresponded exactly to the PCL content in the blend (90 wt %). Similar behavior was observed for the other blends, and this indicated that the first main weight-loss stage of the blends corresponded to the PCL decomposition, which occurred at lower temperatures than observed for the PCL homopolymer.

However, the thermal stability of the blends was gradually raised with an increase in the 3-APTEOS content (Fig. 3). Meanwhile, the percentage of the weight loss was the same as that observed for blends with no 3-APTEOS, which corresponded to the PCL content in the blends. This result showed that Nafion reduced the thermal stability of PCL, whereas the addition of 3-APTEOS diminished the Nafion effect on PCL degradation. PCL is a polyester, and its hydrolysis, catalyzed by acid, is well described in the literature.[20] Nafion possesses SO_3H end groups. The TGA results showed that Nafion caused a reduction in the thermal stability of the blends, suggesting that PCL was hydrolyzed under heating in the presence of Nafion.

An increase in the 3-APTEOS content caused a gradual increase in the thermal stability of the blends with respect to the blends without alkoxysilane. This result, an additional factor indicating the formation of a $—NH_4^+SO_3^-$ complex between Nafion and 3-APTEOS,

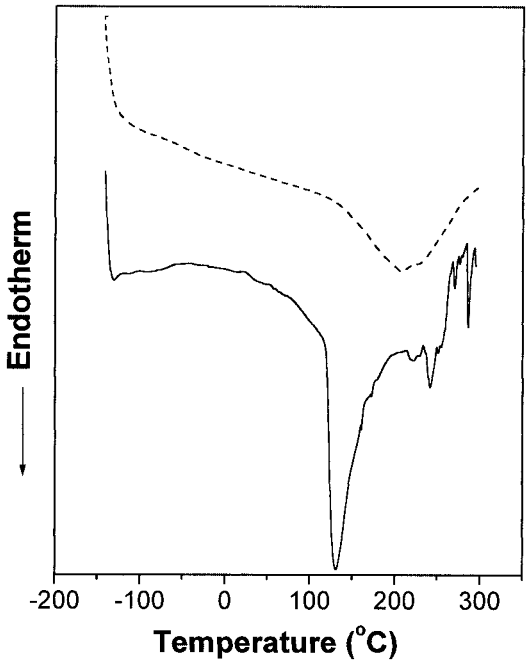
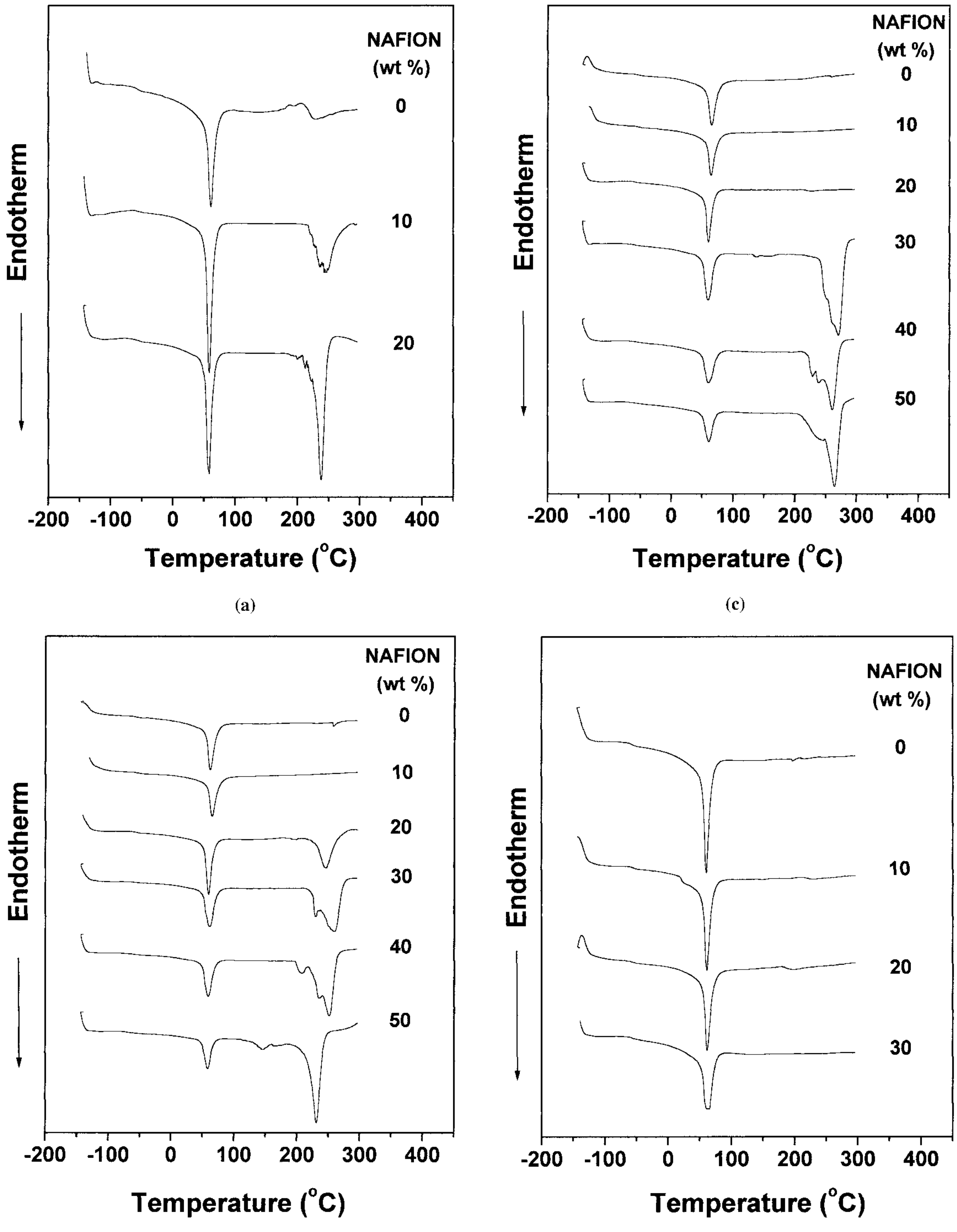


Figure 6 DSC curves for (—) Nafion and (- - -) Nafion containing 10 wt % 3-APTEOS.



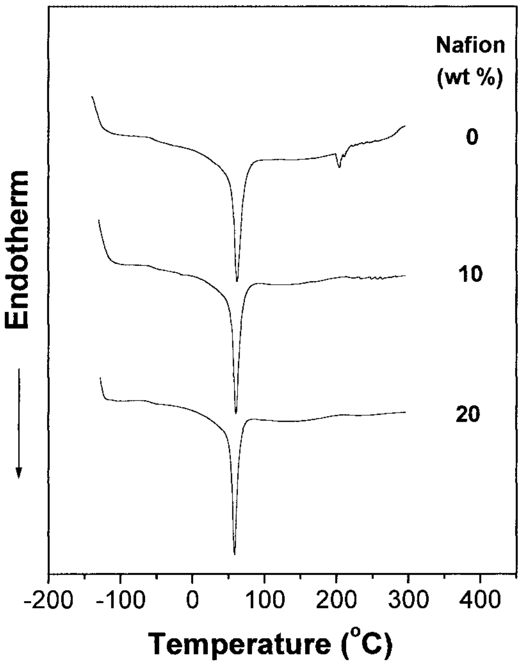
(a) (c) (b) (d)

Figure 7 DSC curves for PCL/Nafion blends containing different 3-APTEOS contents: (a) 0, (b) 1, (c) 2.5, (d) 5, and (e) 10 wt %.

should cause a reduction in the concentration of the free acid groups in Nafion available to attack the PCL chains. For blends containing more than 5 wt % 3-APTEOS, the main weight-loss process occurred at a temperature near that of PCL, and this suggested that at this 3-APTEOS concentration, most of the —SO_3H groups were in the $NH_4^+SO_3^-$ complex.

PAS–FTIR

PAS–FTIR spectroscopy was performed on PCL, Nafion, and a PCL/Nafion (80/20) blend, before and after thermal treatment (Fig. 4), to follow the decomposition reaction of PCL caused by Nafion under heating. In the thermal treatment, the PCL/Nafion (80/20)



(e)

Figure 7 (*Continued from the previous page*)

blend was heated under an argon atmosphere up to 245°C, and it was kept at 245°C for 1 h. This temperature was chosen from the TGA results obtained for the PCL/Nafion blends, and it was lower than the pure PCL degradation temperature, 420°C.

PCL showed the characteristic peaks of a polyester, situated at 1730 cm^{-1},[21] due to a carbonyl group and the stretching mode of C—O in the region between 1100 and 1200 cm^{-1}. The Nafion spectrum showed bands at 971 and 984 cm^{-1}, which were associated with C—O—C stretching vibrations. The band near 1060 cm^{-1} and a shoulder around 1310 cm^{-1} were assigned to symmetric and asymmetric stretching modes of the —SO$_3^-$ group.[22] The photoacoustic spectroscopy spectrum of Nafion showed a strong and broad band from 1100 to 1400 cm^{-1}, which was assigned to stretching vibrations mainly involving the C—F bonds, whereas the bands below 600 cm^{-1} were mainly related to the CF$_2$ angular deformation vibrations.[22,23] The PCL/Nafion (80/20) blend showed the same peaks observed in the pure homopolymers with no displacement; this is expected for immiscible systems. The spectrum of the thermally treated PCL/Nafion (80/20) blend was similar to the Nafion one, and just two large bands, with a low intensity, can be seen at 3000 and 1750 cm^{-1} due to the PCL residue, confirming the degradation of PCL in the blends at lower temperatures than that for pure PCL.

DSC

DSC thermograms obtained for PCL and the hybrids are shown in Figure 5. The pure PCL glass transition occurred at −60°C [Fig. 5(b)]. An endothermic peak, with a maximum observed at 60°C [Fig. 5(a)], was due to the melting of the crystalline PCL phase. The addition of 3-APTEOS caused displacement neither in the glass-transition temperature [Fig. 5(b)] nor in the maximum of the melting peak of PCL [Fig. 5(a)]. In the TEOS/PCL hybrids,[14] a glass-transition-temperature displacement was observed in samples containing about 50 wt % TEOS. In this work, a low content of 3-APTEOS (maximum 10 wt %) was not enough to cause hardening of the hybrids and, consequently, a reduction of the PCL chain mobility.

The crystallinity of the PCL chains was evaluated from the area of the melting peak under the assumption that the fusion heat for pure PCL crystals was 148 J/g (Table I).[24] The correction of the degree of crystallinity with respect to the PCL content in the hybrids was carried out in relation to the total weight, under the assumption that all the 3-APTEOS was converted into silica. The degree of crystallinity of the PCL hybrids practically did not change with the addition of 3-APTEOS.

The Nafion DSC curve is shown in Figure 6. An endothermic peak can be observed, the maximum of which occurs at 131°C, and a second endothermic peak can be observed at 245°C. In the literature,[15] the

TABLE II
DSC Results for PCL/N Blends Containing Different 3-APTEOS Concentrations: Degree of Crystallinity of PCL (x_c) and Melting Temperature (T_m)

PCL (wt %)	3-APTEOS (wt %)									
	0		1		2.5		5		10	
	x_c	T_m	x_c	T_m	x_c	T_m	x_c	T_m	x_c	T_m
100	39	59	38	60	38	60	48	59	41	62
90	56	58	39	65	37	64	52	61	41	60
80	52	58	47	59	42	59	55	65	40	58
70	—	—	53	61	51	59	57	60	—	—
60	—	—	51	59	60	60	—	—	—	—
50	—	—	45	58	60	60	—	—	—	—

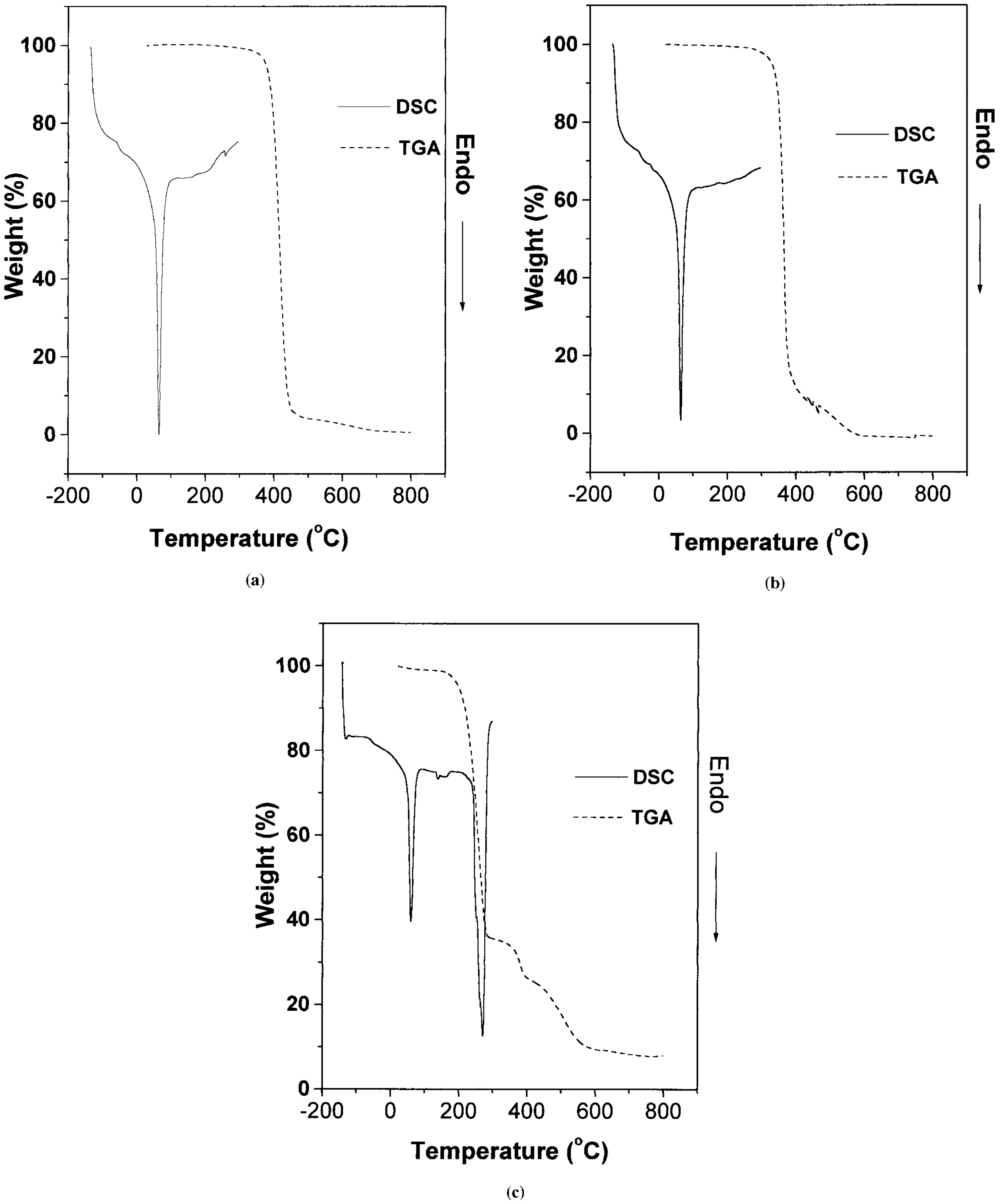


Figure 8 DSC and TGA thermograms for the polymers and blends containing 2.5 wt % 3-APTEOS: (a) PCL hybrid, (b) 90/10 PCL/Nafion, (c) 70/30 PCL/Nafion.

peak at 131°C is related to the polar cluster transition, whereas the peak at 245°C is attributed to the melting of the hydrophobic crystalline phase. In the DSC curve for Nafion containing 10 wt % 3-APTEOS (Fig. 6), only one large endothermic peak can be observed from 130 to 300°C; a maximum can be seen at 200°C. As suggested by the results of the solubility testing and TGA, the addition of 3-APTEOS to the Nafion solution should result in an ionic $NH_4^+SO_3^-$ complex. This ionic interaction should be responsible for the change in the profile of the DSC curve, with respect to pure Nafion, and for the displacement observed in the maximum of the endothermic peak.

From the DSC curves shown in Figure 6, it was not possible to determine the glass-transition temperatures of Nafion and its hybrid.

The Nafion glass-transition temperature and melting temperature are not clearly attributed in the literature. Yeo and Eisenberg[25] assigned a transition near 111°C to the glass-transition temperature of the nonpolar matrix. Another transition around 20°C was attributed to molecular motions within the ionic phase. Stefanithis and Mauritz,[15] investigating Nafion membranes, found a transition near 145°C and another at 230°C. The former was assigned to the polar cluster transition, whereas the latter was attributed to the melting of the nonpolar phase. Laporta et al.[23] reported a glass-transition temperature for Nafion 177 membrane at 130.8°C.

DSC curves for the blends are shown in Figure 7. All the curves show the glass-transition and melting temperatures in ranges similar to those observed for pure PCL, independent of the 3-APTEOS or Nafion contents. This shows that the blends were immiscible over the entire composition range studied. The degree of crystallinity and the melting temperature of blends containing different Nafion and 3-APTEOS contents are shown in Table II. An increase in the Nafion content caused an increase in the degree of crystallinity of blends containing up to 5 wt % 3-APTEOS, whereas the melting temperature practically did not change. Moreover, in the DSC curves of PCL/Nafion blends, an endothermic peak can be observed around 250°C (after the melting of PCL), which is dependent on the Nafion and 3-APTEOS contents. This endothermic process is clearly related to the thermal decomposition of the blends, as can be observed in Figure 8, in which DSC and TGA thermograms are plotted together for blends containing 2.5 wt % 3-APTEOS. In Figure 8(a,b), corresponding to data of PCL and the PCL/Nafion (90/10) blend, the DSC curves show an intense endothermic peak associated with the melting process, and the PCL DSC curve shows a peak of very low intensity around 250°C. As in blends containing higher Nafion contents [Fig. 8(c,d)] a very intense peak can be seen after the PCL melting peak; this peak is coincident with the higher weight loss in TGA.

CONCLUSIONS

Self-supported and macroscopically homogeneous films of PCL/Nafion blends could only be obtained in a wider composition range in the presence of 3-APTEOS.

A Nafion hybrid containing 10 wt % 3-APTEOS was soluble in THF, and this suggested that the alkoxysilane inhibited the formation of the polar clusters present in the Nafion film, which acted as a physical crosslinker.

TGA and DSC results showed that the thermal stability of the PCL/Nafion blends was dependent on both the Nafion and 3-APTEOS contents, which acted in opposite directions. Although the increase in the Nafion content reduced the thermal stability of the blends, the increase in the 3-APTEOS concentration raised it. The first significant weight loss in the blends was attributed to PCL degradation, which occurred at a lower temperature than that observed for pure PCL. All the experimental evidence showed that the PCL degradation occurred by acid hydrolysis caused by the attack of Nafion acid groups under heating. The PCL degradation process in the PCL/Nafion blends was reduced by the addition of 3-APTEOS, being suppressed above 5 wt % alkoxysilane.

DSC results showed that PCL and Nafion were immiscible. The degree of crystallinity of PCL was slightly increased with an increase in the Nafion content, whereas the melting temperature remained about the same.

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