Interactions in Blends Containing Chitosan with Functionalized Polymers

Cristian Castro, Ligia Gargallo, Angel Leiva, Deodato Radić

Departmento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile

ABSTRACT: The phase behavior of blends containing chitosan with poly(vinyl-alcohol) (PVA) and poly(2-hidroxy-ethyl methacrylate) (P2HEM) was analyzed. Blends were obtained by casting from acetic acid solution (HAc) and 1,1,1,3,3,3 hexafluoro-2-propanol (HF2P) and studied by DSC, FT-IR, and TGA. The phase behavior of the blends of chitosan with PVA and P2HEM, studied by DSC, shows that the systems behave as one-phase systems in HAc as well as in HF2P according to the DSC results. According to the results of FT-IR analyses of the different absorptions of the blends, relative to the pure components, they show an important shift that is considered evidence of an interaction between the components of the blends. The thermogravimetric analysis of the blends and the pure components shows that the temperature for thermal degradation of the blends is higher that that of the pure components, irrespective of the solvent casting from which the mixture was obtained. These results are interpreted as the formation of a new product that corresponds to a compatible polymer blend. The compatibilization of these systems is attributed to strong interactions, like hydrogen bonds formation between the functionalized polymers and chitosan, due to the presence of interacting functional groups in all the polymers studied. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1953–1960, 2005

Key words: chitosan; specific interactions; compatibility; FT-IR; thermogravimetric analysis
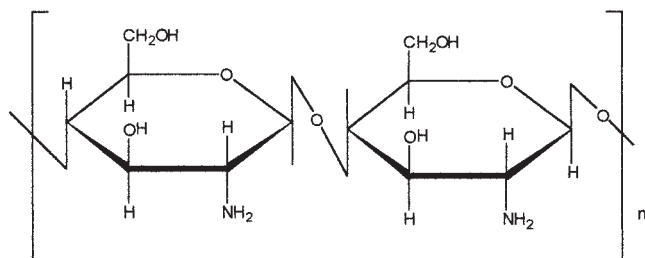
INTRODUCTION

Polymer blends are a matter of active interest in recent years, mainly due to being a versatile way to develop new materials with designed properties that cannot be reached by using single polymers. The development of new useful blends however is severely limited by the incompatibility of many polymer pairs of interest due to entropic reasons.[1–3] Specific interactions, as well as the dilution of repulsive interactions by less favorable ones, can produce negative heats of mixing.[4–7] By this way, the chemical structure of the polymeric components plays an important role in enhancing interactions that can promote miscibility. The role of polymer–polymer interactions in determining the phase behavior and final properties of polymer blend materials is of interest in the prediction of miscibility in polymer blends.[8–10] The use of functionalized polymers represents a good way to obtain interacting polymers that can produce a single-phase material.[8–14] Chitosan can be considered a strongly interacting polymer that can allow one to obtain compatible polymer blends.

Correspondence to: D. Radić (dradic@puc.cl).

Chitosan is a natural polymer, $(1\rightarrow 4)$-2-amino-2-deoxy-β-D-glucan (see Scheme 1), which consists of N-deacetylated derivatives of chitin $(1\rightarrow 4)$-2-acetamido-2-deoxy-β-D-glucan.[15–17] A small amount of free amino groups is generally present in naturally occurring chitin. This natural polymer, which has a similar structure to that of cellulose, presents several functional groups, which are able to interact with other functionalized polymers. In fact, chitosan has four hydroxyl groups, an amine group, and a minor proportion of amide groups, which are, in general, partially hydrolyzed; therefore, some carboxylic acid groups can be present. The importance and applications of chitosan in photography, ophthalmology, agricultural, medical, and food and cosmetic industries have been described elsewhere.[18,19] Modification of chitosan by compatibilization with other polymeric materials could be of interest for different applications.

Compatibility in multifunctional polymers is in general favored by specific interactions, such as hydrogen bonds, dipole–dipole, acid–base, or complexation between the components.[20] These interactions give rise to negative heats of mixture favoring the mixing process.[20–22] The aim of this work is to analyze, by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA), the compatibilization process

Scheme 1

of chitosan with poly(vinyl alcohol) (PVA) and poly(2-hidroxyethyl methacrylate) (P2HEM) and the solvent casting effect on this process.

EXPERIMENTAL

Polymers

Poly(vinyl alcohol), 99+% hydrolyzed, and poly(2-hydroxyethylmethacrylate) (P2HEM) used was a commercial product supplied by Aldrich and has a weight-average molecular weight, M_w = 50,000 and a viscosimetric average molecular weight, M_v = 300,000, respectively.

The chitosan used was a 80% degree of deacetylation sample with, M_V = 360,000. It was a biodegradable natural copolymer obtained by chitin modification.

Preparation of the blends

Blends of different compositions were prepared by solution casting using acetic acid (HAc) solutions and 1,1,1,3,3,3-hexafluoro-2-propanol (HF2P). The polymer concentration in the solution was about 0.7% w/w.

DSC measurements

The glass transition temperatures (T_g) of the pure polymers and blends were measured with a Mettler-Toledo DSC 821 calorimetric system using the STAR[e] program. Polymer samples were dried under reduced pressure in a vacuum oven prior to measurement. Dry nitrogen was used as purge gas and thermograms were measured in the range 223 to 473 K at a scan rate of 20° min^{-1} and 298 to 473 K at a scan rate of 10° min^{-1}.

FT-IR measurements

Infrared spectra of pure polymers and blends were recorded on a Vector 22 Bruker Fourier Transform Infrared Spectrophotometer. The spectra were re-

corded with a resolution of 1 cm^{-1}. The samples were prepared directly in KBr pellets.

TGA measurements

The thermal degradation of the pure polymers and blends was measured with a Mettler TG-50 system equipped with a TC-10A processor using STAR[e] program and thermograms were measured in the range 298 to 1100 K at a scan rate of 20° min^{-1}.

RESULTS AND DISCUSSION

Dry blends of chitosan with PVA and P2HEM were transparent and showed thermograms exhibiting a distinct single glass transition temperature (T_g). Figure 1 shows the DSC curves for blends of chitosan with PVA and P2HEM obtained by casting from HAc as an example and Figure 2 shows the corresponding phase diagrams. A continuous variation of T_g, where values are intermediate between the T_gs of the pure components, is observed. This behavior would indicate miscibility over the whole range of compositions, irrespective of the casting solvent used, i.e., HAc or HF2P. However, the shapes of the blend and curves are rather different depending on the solvent used. The PVA/chitosan blend shows a sinusoidal shape when the blends are cast from HAc, but a curve below the line corresponding to the calculated values from the pure components is observed when the casting solvent is HF2P. On the other hand, in the case of P2HEM/chitosan blend, there is a dramatic change in the shape of the curves. Blends obtained from HAc give T_g values higher than those corresponding to the pure components, while those obtained by casting from HF2P show the opposite behavior. To analyze in a quantitative way the variation of T_g with the blend composition for these systems the Gordon Taylor (GT),[23] Couchman (C),[24] and Kwei (K)[25] treatments of the data were used. The parameters obtained through these equations are considered as semiquantitative measures of the strength of the interaction between the interacting groups of the polymeric components.[26] Table I compiles the Gordon Taylor (K_{GT}), Couchman (K_C), and Kwei (K_{kwei}) constants for the systems studied. These values of K_{GT} and K_C constants would indicate that the interaction between the polymeric components is enough to favor polymer–polymer miscibility. However, the above two first procedures are not the best fitting methods because they cannot describe the S-shaped curves like that of the PVA blend from HAc. These curves can be fitted using the Kwei equation:

$$T_g = \frac{(w1T_{g1} + k_{w2T_{g2}})}{(w1 + k_{w2})} + q_{w1w2}, \tag{1}$$
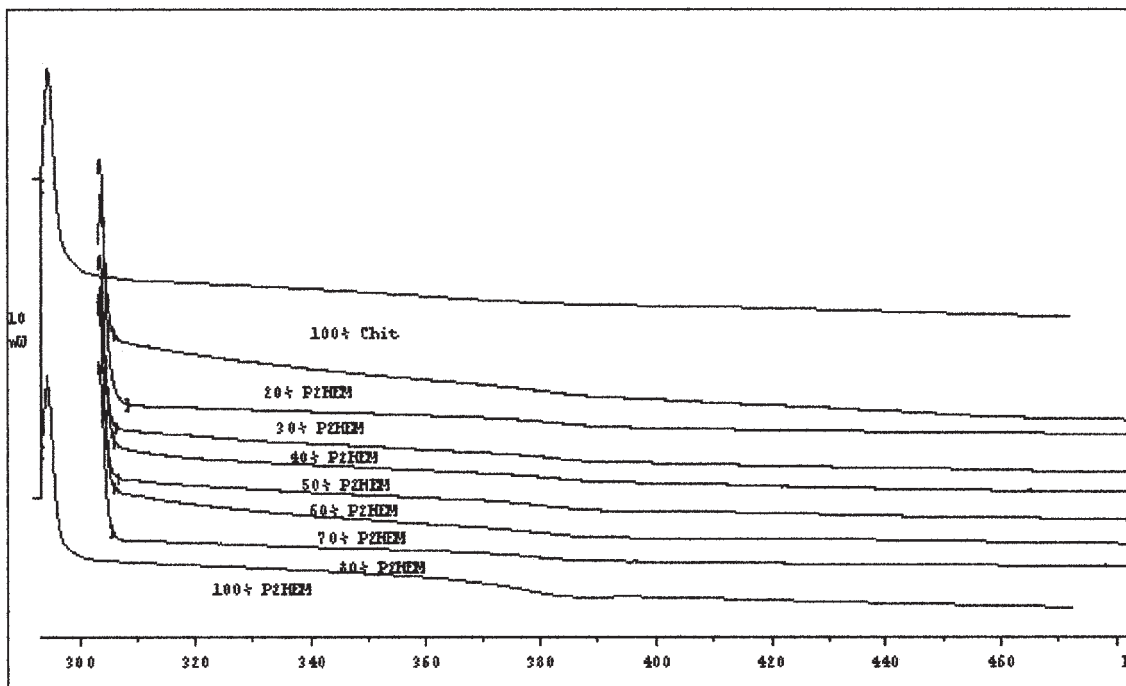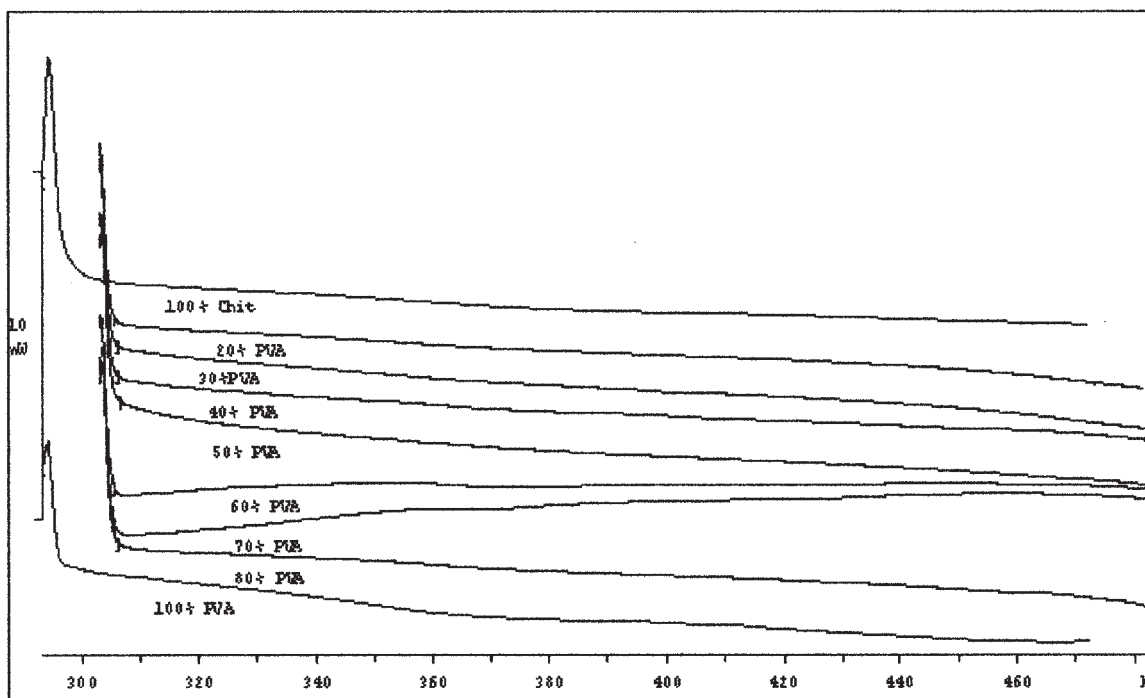
Figure 1 DSC thermograms for the different polymer blends. (a) Curves for the blend P2HEM/chitosan from HAc; (b) curves for the blend PVA/chitosan from HAc.

where w_i are the weight fractions of the components, T_g is the glass transition temperature of the blend, and T_{gi} are the glass transition temperatures corresponding to the pure components. According to these results

it can be assumed that a strong interaction between the components of the blends takes place. Annealed blends show one single enthalpy relaxation peak, which is indicative of miscibility. Miscibility between
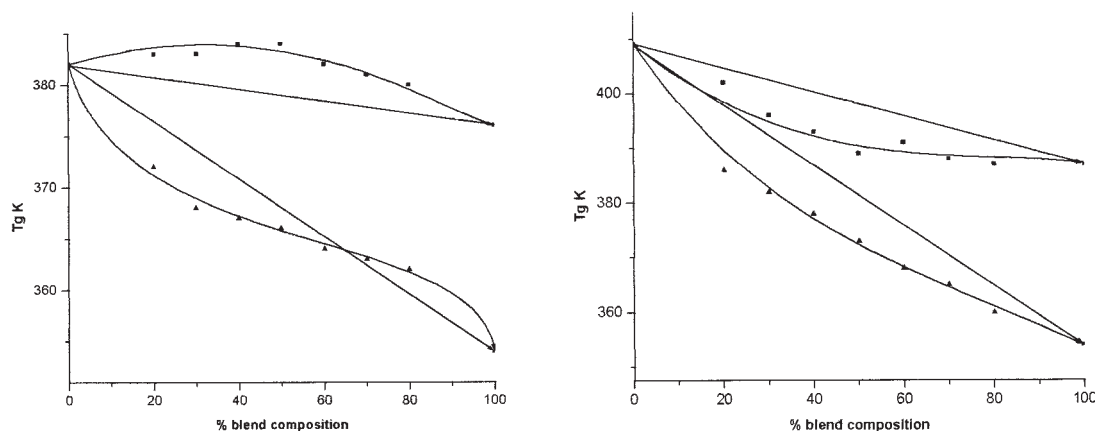
Figure 2 Phase diagrams, T_g versus composition (a) (■) % P2HEM from HAc; (▲) % PVA from HAc; (b) (■) % P2HEM from HF2P; (▲)% PVA from HF2P.

chitosan and PVA or P2HEM can be attributed to hydrogen bonding interaction, taking into account that chitosan is an hydrophilic polymer and PVA and P2HEM are polymers with hydroxyl groups that are able to interact with the amine group or with the hydroxyl groups of chitosan. In fact, these can be considered as interacting polymers due to their functional groups. Therefore, in the case of PVA/chitosan blends, the existence of a one-phase material can be attributed to hydrogen bond interaction betwen the –OH group of PVA with the –OH or –NH$_2$ group of chitosan. A similar explanation could be assumed for the P2HEM/chitosan blend, i.e., the –OH group of P2HEM can interact via hydrogen bond with the –OH or –NH$_2$ groups of chitosan. Nevertheless, preliminary results dealing with molecular simulation seem to indicate that the interactions take place mainly with the –OH groups.
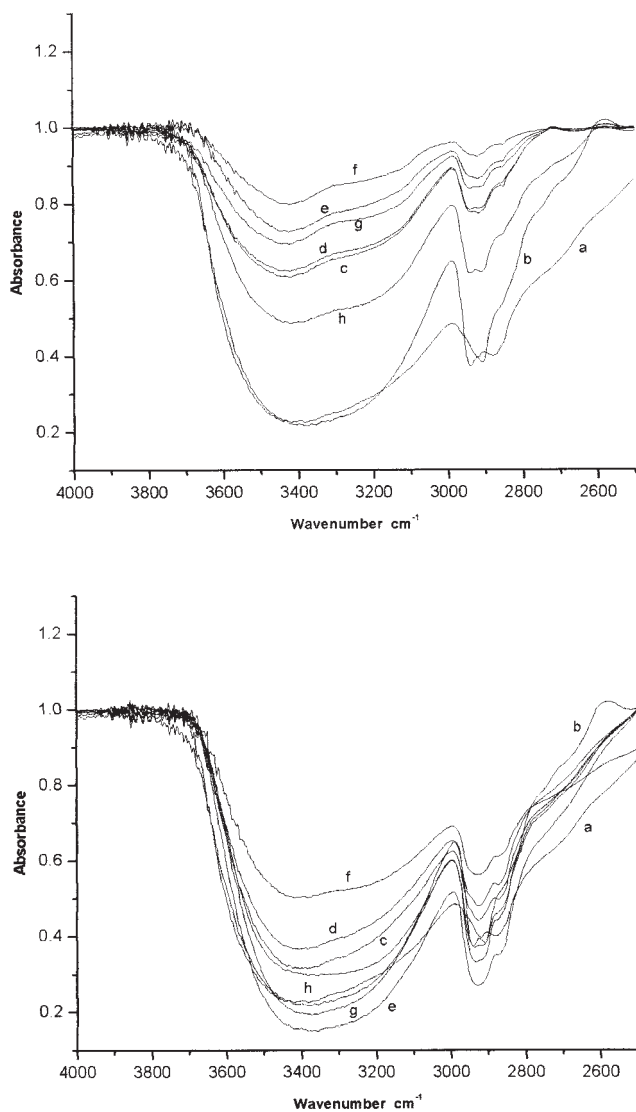
It is difficult to explain the miscibility behavior of the blends depending on the solvent. This result can be attributed to the different thermodynamic power of the casting solvents. HAc is a good solvent for chitosan and HF2P is a poor solvent for chitosan. Therefore the hydrodynamic volume of chitosan in one solvent is different from the other. As a result, the conformation of the polymers in solution should be rather different.

To obtain further information about the interactions involved in the mixing process, FT-IR and thermogravimetry measurements were performed. In general, the shifts of the different absorptions in FT-IR are small.[27] Nevertheless, the results obtained by this technique are generally considered to be complementary with those of calorimetric measurements and thermogravimetry.

FT-IR spectra in the zone of amino and hydroxyl groups were analyzed, using the computer program of the apparatus. Following the absorption at about 3400 cm^{-1} at different blend compositions for the blend chitosan-PVA, it is possible to observe a shift toward higher frequencies than those of the pure chitosan and P2HEM, which could be attributed to the effect of one functional group of one polymer on the functional group of the other. Figures 3(a) and (b) show the FTIR spectra for PVA/chitosan blends in the zone of 3400 cm^{-1} obtained from HAc and HF2P, respectively. Analysis of this region is difficult because the hydroxyl and amino groups of chitosan overlap. Nevertheless it is possible to observe a shift of the whole absorption that could be interpreted as the result of an interaction between the amino and/or hydroxyl groups of chitosan and the hydroxyl of PVA. The shift of the absorption bands in the blends reaches about 47 cm^{-1} for PVA and 39 cm^{-1} for chitosan relative to the pure components in blends obtained by casting from HAc. In the same absorption zone for blends obtained from HF2P, an important shift of the absorption bands also is observed. This is a very important displacement that would indicate strong interactions between the polymeric components.[18,19] These variations in the blends should be the result of compatibilization of the polymers. Therefore, it is possible to assume that a one-phase system is present. This result is in agreement with the previous calorimetric results, which

TABLE I
Couchman (K_C), Gordon-Taylor (K_{GT}) and Kwei (K_{KWEI}) Constants for the Blends of P2HEM and PVA with Chitosan Obtained from HAc and HF2P

Blends	K_C	K_{GT}	K_{KWEI}	q
P2HEM/chitosan from HAc	0.29	0.30	1.76	13.1
PVA/chitosan from HAc	0.23	0.23	0.18	31.6
P2HEM/chitosan from HF2P	0.35	0.34	0.91	−25.8
PVA/chitosan from HF2P	0.46	0.43	0.23	−29.0

Figure 3 FT-IR absorption bands in the 3400 cm^{-1} region for blends of PVA/chitosan obtained from HAc and HF2P, respectively. (a) Blends obtained from HAc: a, chitosan; b, PVA; c, PVA 20%; d, PVA 30%; e, PVA 50%; f, PVA 60%; g, PVA 70%; h, PVA 80% and (b) from HF2P: a, chitosan; b, PVA; c, PVA 20%; d, PVA 30%; e, PVA 40%; f, PVA 50%; g, PVA 60%; h, PVA 70%.

allows us to conclude that miscibility between these systems takes place.
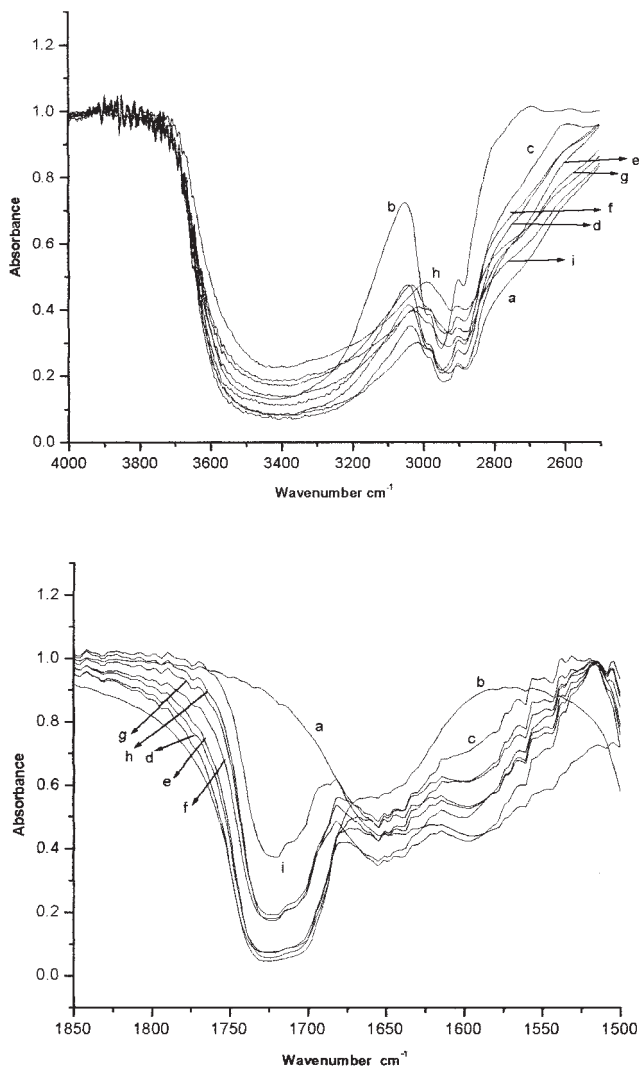
In the case of blends of P2HEM with chitosan the FT-IR analysis shows the same behavior in the sense that results are in agreement with the calorimetric results. Figures 4(a) and (b) show the FT-IR spectra for these blends in the 3400 and 1700 cm^{-1} zones for those systems obtained from HAc. Important shifts of the absorption bands for P2HEM and chitosan are observed. The displacement of the band for P2HEM reaches about 60 cm^{-1} and that corresponding to chitosan reaches 30 cm^{-1}. On the other hand, a small shift of the absorption band of the carbonyl group of

P2HEM is observed in the 1700 cm^{-1} zone. This shift indicates that the carbonyl group of P2HEM is also affected by the interaction with the other polymer. Both results are indicative of strong interaction between the polymers. Similar behavior is observed for P2HEM/chitosan blends obtained by casting from HF2P. Figures 5(a) and (b) show the absorptions in the 3400 and 1700 cm^{-1} zones. The shift of the bonds reaches about 30 cm^{-1} for the 3400 cm^{-1} band and 5 cm^{-1} for the 1700 cm^{-1} band, respectively. All of these results seem to indicate that the blends are miscible over the whole range of compositions.

Another complementary technique to obtain information about the compatibility of the polymers blends
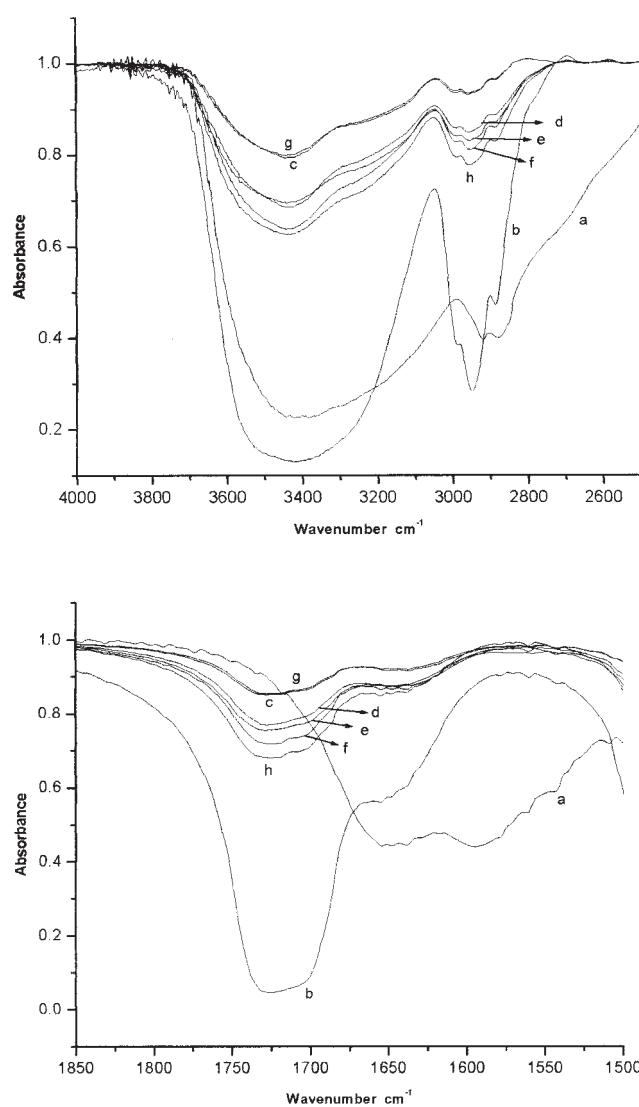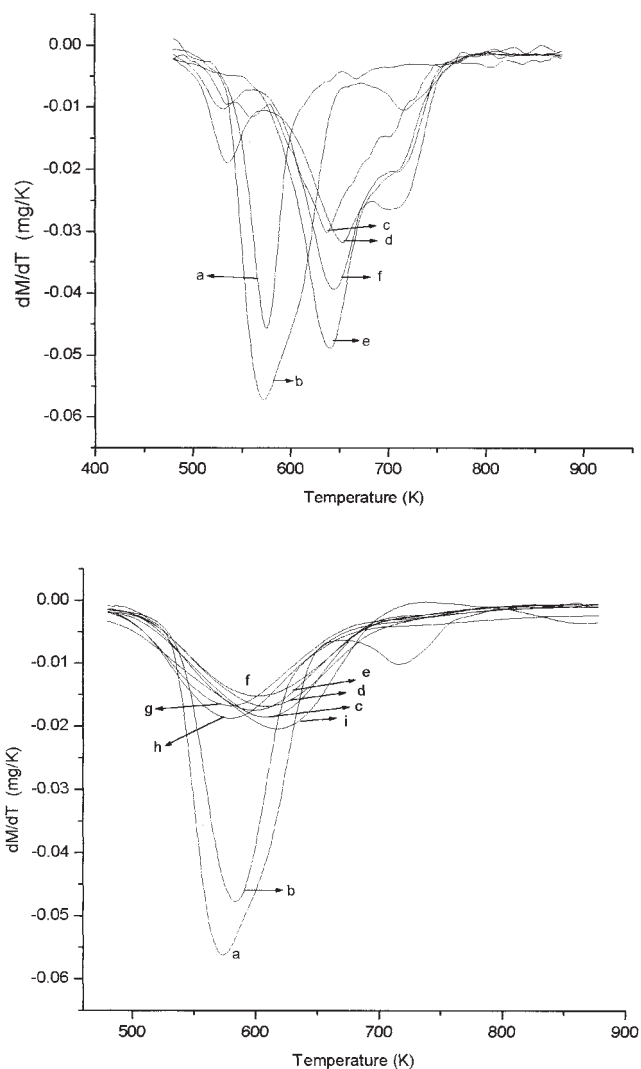

Figure 4 (a) FT-IR absorption bands in the 3400 cm^{-1} region for blends of P2HEM/chitosan obtained from HAc: a, chitosan; b, P2HEM; c, P2HEM 20%; d, P2HEM 30%; e, P2HEM 40%; f, P2HEM 50%; g, P2HEM 60%; h, P2HEM 70% and (b) absorption bands in the 1700 cm^{-1} region for P2HEM/chitosan blends obtained from HAc: a, chitosan; b, P2HEM; c, P2HEM 20%; d, P2HEM 30%; e, P2HEM 40%; f, P2HEM 50%; g, P2HEM 60%; h, P2HEM 70%.

peak, a shoulder at higher temperatures is observed in the systems obtained from HAc. For blends of PVA/chitosan obtained from HF2P, a single one-stage decomposition process is observed. The main observation of these systems is that decomposition of the blends takes place at higher temperatures than those for the degradation of the pure components, irrespective of the blend composition and the casting solvent for the blend. The difference between the degradation temperature for blends relative to the pure components reaches almost 30°, an important difference that would indicate the formation of a new more stable component. This result seems to be another argument indicative that the blend is compatible. In fact, there are new products that degrade at higher temperatures

Figure 5 (a) FT-IR absorption bands in the 3400 cm^{-1} zone for blends of P2HEM/chitosan obtained from HF2P: a, chitosan; b, P2HEM; c, P2HEM 20%; d, P2HEM 30%; e, P2HEM 40%; f, P2HEM 50%; g, P2HEM 60%; h, P2HEM 70%; i, P2HEM 80% and (b) absorption bands in the 1700 cm^{-1} region for P2HEM/chitosan blends obtained from HF2P: a, chitosan; b, P2HEM; c, P2HEM 20%; d, P2HEM 30%; e, P2HEM 40%; f, P2HEM 50%; g, P2HEM 60%; h, P2HEM 70%; i, P2HEM 80%.

is the dynamic thermogravimetric analysis of the pure components and blends of chitosan with PVA and P2HEM.[17] Figures 6(a) and (b) show the degradation profiles for PVA/chitosan blends obtained from HAc solution and HF2P, respectively. These profiles are represented as the first derivative of the weight loss with temperature dM/dT. This kind of representation is a better way to enhance the thermogravimetric behavior to observe the degradation temperature than the diagrams of pure weight loss versus temperature.[10] These thermogravimetric profiles follow a single one-stage decomposition process for pure polymers. For the blends, besides the main degradation

Figure 6 (a) Thermogravimetric profiles for PVA/chitosan blends obtained from HAc: a, PVA; b, chitosan; c, PVA 50%; d, PVA 60%; e, PVA 70%; f, PVA 80%. (b) Thermogravimetric profiles for PVA/chitosan blends obtained from HF2P: a, PVA; b, chitosan; c, PVA 20%; d, PVA 30%; e, PVA 40%; f, PVA 50%; g, PVA 60%; h, PVA 70%; i, PVA 80%.
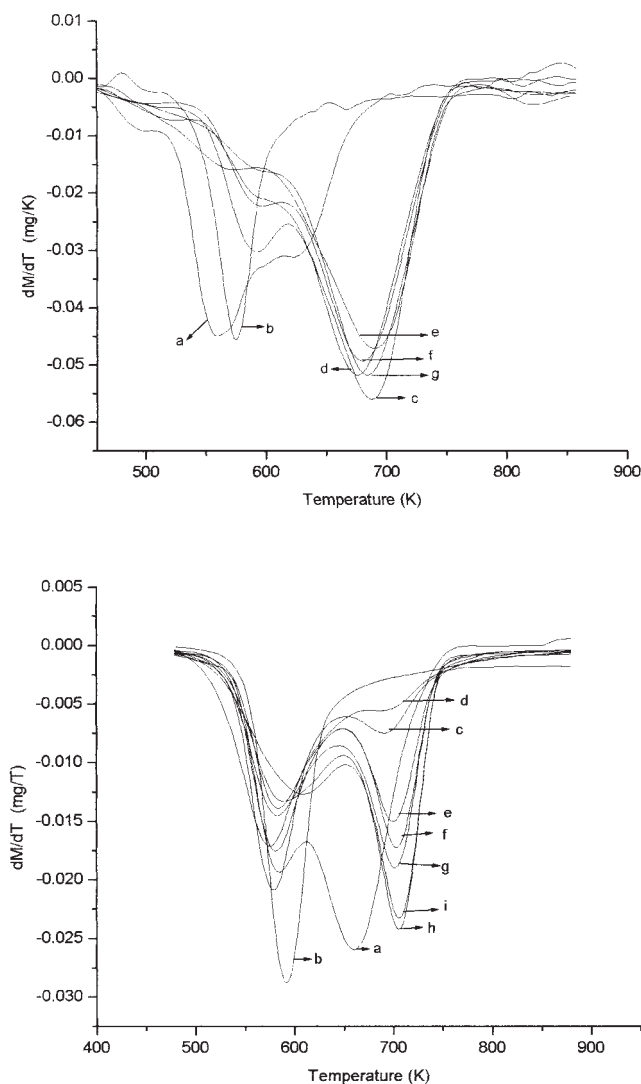
Figure 7 (a)Thermogravimetric profiles for P2HEM/chitosan blends obtained from HAc: a, P2HEM; b, chitosan; c, P2HEM 30%; d, P2HEM 40%; e, P2HEM 50%; f, P2HEM 70%; g, P2HEM 80%. (b) Thermogravimetric profiles for P2HEM/chitosan blends obtained from HF2P: a, P2HEM; b, chitosan; c, P2HEM 20%; d, P2HEM 30%; e, P2HEM 40%; f, P2HEM 50%; g, P2HEM 60%; h, P2HEM 70%; i, P2HEM 80%.

than the pure components. Therefore, it is possible to assume that the new product, which would correspond to a compatible polymer blend, has thermal stability higher than that of the pure polymers. The presence of two degradation profiles for some blends would indicate that, in these particular cases, the blend could constitute a compatible polymer blend with a fraction of pure components that decompose at their own degradation temperature. This means that the blend could be partially compatible or, depending on the composition, there is not enough material to interact and to behave as one single component. Nevertheless, the formation of a new product is inferred

with a higher degradation temperature than that of the pure components, i.e., there is an enhancement of the thermal stability due to the blending process. Figures 7(a) and (b) represent the degradation profiles for the decomposition of blends of P2HEM with chitosan obtained by casting from HF2P. As in the case of PVA/chitosan blends, the blends of P2HEM/chitosan show that the degradation of the blends takes place at higher temperatures than that of the pure components. This fact is indicative that the blend is compatible.

CONCLUSIONS

Blends of chitosan with PVA and P2HEM obtained from HAc as well as HF2P seem to be compatible. This conclusion is reached by the analysis of the calorimetric results, i.e., all the blends show a single T_g value and the interaction constants obtained by the Gordon-Taylor, Couchman, and Kwei procedures show that strong interactions should take place. The FT-IR and thermogravimetric analyses of the different blends indicate the same conclusion. According to these results, taking into account the chemical structure of the polymers, the interaction between the polymers can be attributed to hydrogen bonding formation.

References

1. Lu, X.; Weiss, R. A. Macromolecules 1991, 24, 4381.
2. Paul, D. R.; Newman, S., Eds.: Polymer Blends; Academic Press: Orlando, FL, 1978.
3. Brus, J.; Dybal, J.; Schmidt, P.; Kratochvil, J.; Baldrian, J. Macromolecules 2000, 33, 6448.
4. Ng, C.-W. A.; MacNight, W. Macromolecules 1996, 29, 2412.
5. Cowie, J. M. G.; Elexpuro, E. M.; McEwen, I. J. J Polym Sci Polym Phys 1991, 29, 407.
6. Kambour, R. P.; Bendler, J. T.; Boop, R. C. Macromolecules 1983, 16, 753.
7. Ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. Macromolecules 1983, 16, 1827.
8. Luo, X.; Goh, S. H.; Lee, S. Y. Macromolecules 1997, 30, 4934.
9. Urzúa, M.; Gargallo, L. Radic´, D. J Macromol Sci Phys 2000, B39, 143.
10. Urzúa, M.;. Opazo, A.; Gargallo, L. Radic´, D. Polym Bull 1998, 40, 63.
11. Cowie, J. M. G.; Guang Xian, L.; Ferguson, R.; McEwen, I. J. J Polym Sci Polym Phys 1992, 30, 1351.
12. Brannock, G. R.; Paul, D. R. Macromolecules 1990, 23, 5240.
13. Cowie, J. M.G.; Lath, D. Makromol Chem Macromol Symp 1988, 16, 103.
14. Shiomi, T.; Imai, K. Polymer 1991, 32, 73.
15. Majeti, N. V.; Ravi, K. React Funct Polym 2000, 46, 1.

16. Rhazi, M.; Desbrières, J.; Taloimate, A.; Rinaudo, M.; Vottero, P.; Alagui, A.; El Meray, M. Eur Polym Mater 2002, 38, 1523.

17. Desbrières, J.; Martínez, C.; Rinaudo, M. Int J Biol Macromol 1996, 19, 21.

18. Ratto, J.; Hatakeyama, T. Polymer 1995, 36, 2915.

19. Muzzarelli, R.; Jeniaux, C.; Gooday, G. W. Chitin in Nature and Technology; Plenum Press: New York, 1985.

20. Urzúa ,M.; Gargallo, L.; Radic´, D. J Appl Polym Sci 2002, 84, 1245.

21. Brannock, G. R.; Barlow, J. W.; Paul, D. R. J Polym Sci Polym Phys 1991, 29, 413.

22. Paul, D. R.; Barlow, J. W.; Keskkula, H.; Mark-Bikales-Overberger-Menges: Encyclopedia of Polymer Science and Engineering, 2nd ed.; John Wiley: New York, 1988; Vol.12, p 399.

23. Gordon, M.; Taylor, J. J Appl Chem 1952, 2, 493.

24. Couchman, P. R. Polym Eng Sci 1984, 24, 135.

25. Kwei, T. K. J Polym Sci Polym Lett 1984, 22, 307.

26. Belorgey, G.; Prud'Homme, R. J Polym Sci Polym Phys 1982, 20, 191.

27. Pawlak, A.; Mucha, M. Thermochim Acta 2003, 396, 153.