

Experimental and Theoretical Approaches to Investigating the Miscibility of Anhydride-Containing Copolymers and Dextran

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ABSTRACT: The miscibility behavior of dextran (Dx) with synthesized functional binary poly(citraconic anhydride-acrylamide) (poly(CA-*alt*-AAM)) and ternary poly(citraconic anhydride-acrylamide-vinyl acetate) (poly(CA-*co*-AAM-*co*-VA)) copolymers was investigated in dilute aqueous solutions by viscometry and in a solid state by Fourier transform infrared (FTIR) spectroscopy. The relative viscosities of each polymer and their blends with Dx/related copolymer ratios of 20 : 80, 50 : 50, and 80 : 20 were measured at body temperature, 37°C, in bidistilled and deionized water. Starting with the classical Huggins equation, results of the viscosity measurements of each parent polymer and their blends were interpreted in terms of miscibility parameters:

Δk , Δb , α , β , ΔB , and μ . Based on the sign convention used with these criteria, the miscibility between Dx and related copolymers was found to increase with the weight fraction of Dx in the blends and with the number of AAM units in the copolymer composition. From FTIR spectral analysis, supporting results were achieved that explained the interactions between Dx and the copolymers. Miscibility behavior was also investigated theoretically with Askadskii's miscibility criterion, and the theoretical calculations provided strong evidence supporting the experimental results. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2132–2141, 2006

Key words: miscibility; blends; viscosity; FT-IR

INTRODUCTION

In the search for new polymeric materials, either new monomers are polymerized or a copolymerization technique is used to tailor-make a new product. An alternative method has been to blend existing polymers to produce materials with desired properties. An obvious advantage of this approach is that it usually requires little or no extra capital expenditure relative to the new polymers.

The miscibility between the constituents of a polymer mixture is an important factor in the development of new materials based on polymeric blends.¹ In miscible polymeric blends there are often specific interactions between groups or polymer segments that lead to decreased Gibbs energy of mixing. The final properties of polymer blends are directly related to their degree of miscibility.

To investigate polymer–polymer miscibility, the most useful and powerful techniques are electronic microscopy, spectroscopy, thermal analysis, and inverse gas chromatography.² However, most of these techniques are very expensive. An alternative method

for analyzing polymer miscibility in solution that is simple, inexpensive, and reliable is the viscometric technique. In addition, the dilute-solution viscometry method provides information about both polymer–polymer and polymer–solvent interactions in solution. The dilute-solution viscometry method is believed to be effective because of the mutual interactions of macromolecules in solution have a great influence on the viscosity of ternary systems. Researchers have proposed many criteria as determinants of the miscibility of ternary polymer solutions (polymer 1/polymer 2/solvent) by the viscometry method including intrinsic viscosity–composition plots, the interaction parameter (μ), the thermodynamic parameter (α), and the modified thermodynamic parameter (β).^{3–5}

Polymers and oligomers containing reactive functional groups are vitally important in polymer science. Polymers containing epoxy, hydroxy, isocyanate, amine, and carboxylic acid groups are widely used commercially in applications such as pharmaceuticals, protective coatings, adhesives, and composites. Functional groups can also be used to modify such properties of a polymer as adhesion.⁶

It is known that water-soluble anhydrides containing copolymers as polyanions and their functional derivatives have high biological and physiological activity, specially antimicrobial and antitumor properties.^{7,8} Polyanions are also known for their potential to

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simulate the immune system and to invoke activity against tumors, viruses, and bacteria.^{8,9} It has been reported that yet another mode of their action is to induce interferon.¹⁰ Dextran (Dx) is a naturally occurring nontoxic biodegradable polymer. Dextran and its derivatives are used as plasma expanders,¹¹ blood substitutes,¹² and bone-healing promoters¹³ and also for dermal and subcutaneous augmentation.¹⁴ Furthermore, dextran has been widely investigated as a polymeric carrier in novel drug delivery systems.¹⁵⁻¹⁷

In this work, the miscibility between Dx and free-radical-polymerized functional binary and ternary copolymers of citraconic anhydride (CA) was investigated. Studying the molecular interactions between these polymers is important for technology, especially for biomedical and pharmaceutical applications, because of the above explained properties. To investigate the miscibility behavior of Dx and citraconic anhydride-containing copolymers, we chose dilute solution viscometry as the most suitable technique because it provides information on miscibility at the molecular level.

Theoretical

Miscibility parameters based on the viscometry

Basically, the miscibility parameters obtained by dilute solution viscometry were derived from the classical Huggins equation,¹⁸ which expresses the specific viscosity, η_{sp} , of a single-solute solution as a function of concentration, c :

$$\eta_{sp} = [\eta]c + bc^2 \quad (1)$$

where $[\eta]$ is the intrinsic viscosity and b is related to the Huggins coefficient, k_H , by

$$b = k_H[\eta]^2 \quad (2)$$

The value of the Huggins coefficient is a measure of the interpenetration of polymer coils, the extent of which depends on segment-segment and segment-solvent interactions. This, in turn, affects the inter-

molecular hydrodynamic interaction and molecular dimensions.

Krigbaum and Wall¹⁹ adapted Huggins equation to a ternary system, namely, a mixture of two polymers in a common solvent as given below:

$$\eta_{sp,m} = [\eta]_m c_m + b_m c_m^2 \quad (3)$$

where

$$b_m = w_1^2 b_{11} + w_2^2 b_{22} + w_1 w_2 b_{12} \quad (4)$$

where w_1 and w_2 are the weight fractions of polymer 1 and 2; b_{11} , b_{22} , and b_{12} are the terms characterizing the interactions of the same (1-1, 2-2) and different (1-2) polymer molecules, respectively; and

$$b_m = k_m [\eta]_m^2 \quad (5)$$

$$b_{11} = k_{11} [\eta]_1^2 \quad (6)$$

$$b_{22} = k_{22} [\eta]_2^2 \quad (7)$$

$$b_{12} = k_{12} [\eta]_1 [\eta]_2 \quad (8)$$

$$[\eta]_m = [\eta]_1 w_1 + [\eta]_2 w_2 \quad (9)$$

where k_{12} is the Huggins coefficient between different (1-2) polymer molecules. Note that k_{12} and b_{12} are different from k_m and b_m .

Many miscibility parameters have been proposed by researchers to determine polymer-polymer miscibility by the viscometric method such as Δk ,¹⁹ Δb ,¹⁹ α ,³ β ,⁴ ΔB ,⁵ and μ .⁵ The common point of all these parameters is that the miscibility parameter should appear to be greater than zero for the observation of miscibility. For miscibility to occur, larger, positive numbers will represent the phenomenon more clearly.

The equations used to calculate all the above-mentioned miscibility parameters (Δk , Δb , α , β , ΔB , and μ) are summarized in Table I. A more detailed analysis of these equations can be found in a previous work of ours.²⁰

TABLE I
Summary of Equations of Miscibility Parameters (Δb , Δk , α , β , ΔB , and μ)

i)	$\Delta b = (b_{12})_{\text{exp}} - (b_{12})_{\text{theo}}$;	$(b_{12})_{\text{exp}} = [b_m - (b_{11}w_1^2 + b_{22}w_2^2)]/2w_1w_2$ $(b_{12})_{\text{theo}} = (b_{11}b_{22})^{1/2}$
ii)	$\Delta k = (k_{12})_{\text{exp}} - (k_{12})_{\text{theo}}$;	$(k_{12})_{\text{exp}} = [b_m - (b_{11}w_1^2 + b_{22}w_2^2)]/2[\eta]_1[\eta]_2w_1w_2$ $(k_{12})_{\text{theo}} = (k_{11}k_{22})^{1/2}$
iii)	$\alpha = k_m - k_{m1}$;	k_m is the experimentally obtained Huggins constant $k_{m1} = (k_{11}[\eta]_1^2w_1^2 + k_{22}[\eta]_2^2w_2^2 + 2(k_1k_2)^{1/2}[\eta]_1[\eta]_2w_1w_2)/(w_1[\eta]_1 + w_2[\eta]_2)^2$
iv)	$\beta = 2\Delta k[\eta]_1[\eta]_2w_1w_2/(w_1[\eta]_1 + w_2[\eta]_2)^2$;	$\Delta k = (k_{12})_{\text{exp}} - (k_{12})_{\text{theo}}$
v)	$\Delta B = (b_m - \mathfrak{B})/2w_1w_2$;	$\mathfrak{B} = w_1b_{11} + w_2b_{22}$
vi)	$\mu = [(b_m - b_{11})/([\eta]_m - [\eta]_1) - (b_{22} - b_{11})/([\eta]_2 - [\eta]_1)]/2([\eta]_2 - [\eta]_1)$		

Askadskii's miscibility criterion

Solubility parameters, δ , are often used in industry to predict the miscibility of polymers. Moreover, the usefulness of polymers in many technological applications is critically dependent on solubility parameters.²¹ The surface tension, γ , must be known, and it is also important to be able to predict it on the basis of the chemical structure of the substance because many individual properties of liquids and solids, as well as their miscibility and solubility in each other, depend on the surface tension of liquids and the surface tension energy of solids. Askadskii²² improved a criterion that contains both the solubility and surface tension values of polymer pairs in order to investigate their miscibility. Before going into detail about Askadskii's miscibility criterion, some definitions and formulas must be given:

$$\delta^2 = \frac{\Delta E^*}{N_A \sum \Delta V_i} = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i} \quad (10)$$

where N_A is Avogadro's number, ΔE^* is the cohesive energy of the repeat unit of the polymer, and ΔV_i is the (van der Waals) volume that each atom makes up in the repeating unit of the polymer. The value

$$\gamma_p = (\alpha_1 C_{j,1} + \alpha_2 C_{j,2} + \dots) \frac{\alpha_1 (\sum_i \Delta E_i^*)_1 + \alpha_2 (\sum_i \Delta E_i^*)_2 + \dots}{[\alpha_1 (\sum_i \Delta V_i)_1 + \alpha_2 (\sum_i \Delta V_i)_2 + \dots]^{2/3} (\alpha_1 m_1 + \alpha_2 m_2 + \dots)^{1/3}} \quad (13)$$

where all designations are identical to the above-mentioned formulas.

One possible way of looking at the problem of predicting the miscibility of polymers is Askadskii's miscibility criterion, which is intended for use in analyzing the miscibility of polymers as their solubility in each other. If one polymer is introduced in small amounts into another polymer, the former is considered the polymer and the latter the solvent when this criterion is applied. In principle, two variants are probable:

Case I. When small quantities of the first polymer (polymer 1) are introduced into the second one (polymer 2), Askadskii's miscibility criterion is written as:

$$\frac{\delta_{p,1}^2}{\delta_{p,2}^2} 1.374 \Phi \left(\Phi - \sqrt{\Phi^2 - 1 + a_1} \right) \quad (\text{criterion } i)$$

where $\delta_{p,1}$ and $\delta_{p,2}$ are the solubility parameters of polymers 1 and 2, respectively, and

$$a_1 = [\gamma_{p,1} + \gamma_{p,2} - 2\Phi(\gamma_{p,1} \cdot \gamma_{p,2})^{1/2}] \quad (14)$$

$$\Phi = \frac{4(V_{p,1} \cdot V_{p,2})^{1/3}}{(V_{p,1}^{1/3} + V_{p,2}^{1/3})^2} \quad (15)$$

of ΔE^* is additive, and ΔE_i^* is the contribution of each atom and type of intermolecular interaction to ΔE^* . The ΔE_i^* and ΔV_i of many possible interactions and atoms and their detailed analyses of all the above- and below-mentioned equations can be found in Askadskii.²²

Eq. (10) can be rewritten for copolymers as

$$\delta^2 = \frac{\alpha_1 (\sum_i \Delta E_i^*)_1 + \alpha_2 (\sum_i \Delta E_i^*)_2 + \dots}{N_A [\alpha_1 (\sum_i \Delta V_i)_1 + \alpha_2 (\sum_i \Delta V_i)_2 + \dots]} \quad (11)$$

where $\alpha_1, \alpha_2, \dots$ are the molar parts of polymers 1, 2, \dots and $\sum_i \Delta E_i^*$ and $\sum_i \Delta V_i$ are the total cohesive energy and van der Waals volume, respectively, of each component.

The surface tension of polymers (γ_p) is given by:

$$\gamma_p = C_j \frac{\sum_i \Delta E_i^*}{(\sum_i \Delta V_i)^{2/3} m^{1/3}} \quad (12)$$

where m is the number of atoms in the repeat unit of the polymers, and C_j is a constant equal to 0.0476 for polymers like ours.

For copolymers, eq. (12) is rewritten as:

where $V_{p,1}$ and $V_{p,2}$ are the molar volumes of polymers 1 and 2, respectively, and are given by;

$$V_{p,i} = \frac{N_A \sum_i \Delta V_i}{0.681} \quad (16)$$

For copolymers, molar volume can be calculated by

$$V_{p,i} = \frac{N_A [\alpha_1 (\sum_i \Delta V_i)_1 + \alpha_2 (\sum_i \Delta V_i)_2 + \dots]}{0.681} \quad (17)$$

According to Askadskii's miscibility criterion, miscibility will be observed when the right-hand side of the criterion is greater than the left-hand side, with both sides calculated on the basis of the chemical structures of the repeat units of the polymers.

Case II. When small quantities of polymer 2 are introduced into polymer 1, Askadskii's miscibility criterion is written as

$$\frac{\delta_{p,2}^2}{\delta_{p,1}^2} < 1.374 \Phi \left(\Phi - \sqrt{\Phi^2 - 1 + a_2} \right) \quad (\text{criterion } ii)$$

where

$$a_2 = [\gamma_{p,1} + \gamma_{p,2} - 2\Phi(\gamma_{p,1} \cdot \gamma_{p,2})^{1/2}]/\gamma_{p,1} \quad (18)$$

If the left side of criterion II is smaller than the right side, this means the two polymers are miscible with each other, as with the introduction of polymer 2 into polymer 1.

EXPERIMENTAL

Chemicals

Dextran, Dx ($M_n = 6.400$ g/mol), was supplied from Pharmacia (Uppsala, Sweden). Bidistilled and deionized water having almost zero conductivity was used as solvent in the viscosity studies. Characteristics of monomers and solvents used during the copolymerization reactions can be found in a previous study of ours.²³

Copolymerization and terpolymerization

Details of the synthesis of binary CA-AAm copolymers and ternary CA-AAm-VA copolymer were presented previously.²³ For the synthesized copolymers of citraconic anhydride, we used sample codes to prevent possible confusions. These sample codes, elemental analysis results giving co- and terpolymer composition, and some other characteristics of the studied copolymers were summarized as follows:

Copolymer 1 (sample code = **Co1**): yield 53%, acid number (AN) = 244.4 mg KOH/g, % crystallinity < 5, $[\eta] = 0.1037$ dL/g in H₂O at 37°C, monomer unit ratio in copolymer ($m_1:m_2$) = 1:1.18.

Copolymer 2 (sample code = **Co2**): yield 55%, AN = 140.3 mg KOH/g, $[\eta] = 0.1576$ dL/g in H₂O at 37°C, ratio of monomer units in copolymer ($m_1:m_2$) = 1:2.33.

Terpolymer (sample code = **Ter**): yield 30%, AN = 308.6 mg KOH/g, % crystallinity < 5, $[\eta] = 0.0897$ dL/g in H₂O at 37°C, ratio of monomer units in copolymer ($m_1 : m_2 : m_3$) = 4.86 : 1 : 2.47, where m_1 , m_2 , and m_3 are CA, AA, and VA, respectively.

Viscosity measurements

The relative viscosity of both the binary (polymer 1/solvent) and the ternary (polymer 1/polymer 2/solvent) solutions of Dx and citraconic anhydride containing co- and terpolymers were measured at body temperature, 37°C, using a Ubbelohde-type capillary viscometer. Viscosity measurement was carried out in a water bath whose temperature was kept constant within $\pm 0.1^\circ\text{C}$ sensitivity by an electronically controlled thermostat. Solutions of each binary and ternary system were made by dissolving polymer samples at a polymer concentration of 0.8 g/dL. The viscosity of five polymer solutions

with varied compositions of Dx and related copolymers—0 : 100, 20 : 80, 50 : 50, 80 : 20, and 100 : 0—was measured. Dilutions to produce at least five lower concentrations were made by adding solvent. Measurement started after being at equilibrium for 10 min. The average elution time of each solutions was determined from several measurements.

FTIR measurements

Fourier transform infrared (FTIR) spectra of KBr pellets of the samples regenerated by solvent evaporation at room temperature from their aqueous solutions with a concentration of 0.8 g/dL (the same concentration as that for the viscosity measurements) were taken by a Mattson 1000 FTIR spectrophotometer in the 4000–400 cm^{-1} range, where 40 scans were taken at a resolution of 16 cm^{-1} .

RESULTS AND DISCUSSION

Viscometric analysis

Anhydride-containing polymers are technologically important especially for biomedical and pharmaceutical applications. We previously reported details of the synthesis and characterization of binary and ternary copolymers of citraconic anhydride.^{23,24}

The intercept and gradient of the $\eta_{sp,m}/C$ versus C curves were calculated by linear regression, which gave the intrinsic viscosity, $[\eta]$, and Huggins slope coefficient, $b = k_H[\eta]^2$. For all binary and ternary systems studied, reduced viscosity was found to be a linear function of concentration, with correction coefficients of at least 0.98 and no crossovers appearing within the concentration range used ($0.45 < C < 0.8$ g/dL). The results obtained by linear regression analysis and other parameters calculated from the equations mentioned above are summarized in Table II. As can be seen in Table II, the intrinsic viscosity of the blend samples varied between those of the pure polymers, indicating intermolecular interactions between the unlike polymer segments when mixed together.²⁵

For simplicity and to show a comparison of the miscibility behavior of different blends of the polymers studied, Figure 1(a–f) depicts the miscibility parameters presented in Table II as a function of the weight fraction of Dx in the blend samples. As can be seen in Figure 1(a–f), the values of the miscibility parameters did not always agree. In some cases, one miscibility parameter tended to indicate miscibility, whereas another indicated immiscibility. In cases when this contradiction was observed, the blend had not been assigned according to ΔB and μ parameters. Generally, different values were obtained for ΔB and μ than for the other miscibility parameters for the

TABLE II
Viscometric and Thermodynamic Data for Blend Systems

Blend system	W_{Dx}	b (dL/g) ²	$[\eta]_m$ (dL/g)	Δb	Δk	α	β	ΔB	μ
Dx/Co1	1.0	0.0051	0.0790	—	—	—	—	—	—
	0.8	0.0057	0.0830	0.00054	0.06643	0.04314	0.02472	0.00044	1.37398
	0.5	0.0061	0.0915	-0.00019	-0.02359	-0.01398	-0.01158	-0.00030	-0.53760
	0.2	0.0066	0.0975	-0.00096	-0.11667	-0.01942	-0.03136	-0.00106	-1.18555
	0.0	0.0074	0.1037	—	—	—	—	—	—
Dx/Co2	1.0	0.0051	0.0790	—	—	—	—	—	—
	0.8	0.0070	0.0957	0.00324	0.25987	0.09950	0.11540	0.00281	0.40516
	0.5	0.0075	0.1188	0.00022	0.01791	0.00346	0.00797	-0.00020	-0.04268
	0.2	0.0088	0.1410	-0.00051	-0.04133	-0.00271	-0.00818	-0.00094	-0.11855
	0.0	0.0101	0.1576	—	—	—	—	—	—
Dx/Ter	1.0	0.0051	0.0790	—	—	—	—	—	—
	0.8	0.0052	0.0812	0.00019	0.02659	0.00799	0.00916	0.00019	1.57429
	0.5	0.0050	0.0848	-0.00040	-0.00563	-0.03548	-0.02804	-0.00040	-3.66663
	0.2	0.0049	0.0890	-0.00112	-0.15862	-0.06743	-0.04692	-0.00113	-27.6368
	0.0	0.0053	0.0897	—	—	—	—	—	—

blends studied. Sun et al.³ observed that the sign of ΔB and μ could differ for the same polymer blend, which means Chee's approach to estimating polymer miscibility is ambiguous. Despite these contradictions, a common trend was observed with all miscibility parameters. For the studied systems, the miscibility of Dx with related binary and ternary copolymers of citraconic anhydride showed a tendency to increase with the weight fraction of Dx in the blend samples. As can be seen from the miscibility curves, all the miscibility parameters of the Dx/related copolymer blends with a 20 : 80 composition were negative at the studied temperature, suggesting these blend systems may be immiscible. In contrast, all the miscibility parameters of the 80 : 20 Dx/related co-

polymer blends were positive, indicating that Dx and related copolymers mixed in an 80 : 20 ratio are miscible with each other.

Before detailing the miscibility behavior of Dx and related copolymers (Co1, Co2, and Ter), we must first mention to some important characteristics of the studied polymers. The synthesized binary and ternary copolymers are easily dissolved in water. This dissolution process is accompanied by full hydrolysis of anhydride units and formation of strong H-bonding fragments.²⁶ It is known that maleic acid copolymers easily form intramolecular H-bonds with different dissociation constants for two carboxylic groups ($pK_1 > pK_2$).²⁷ The same reaction of the opening anhydride ring also partially proceeded in the

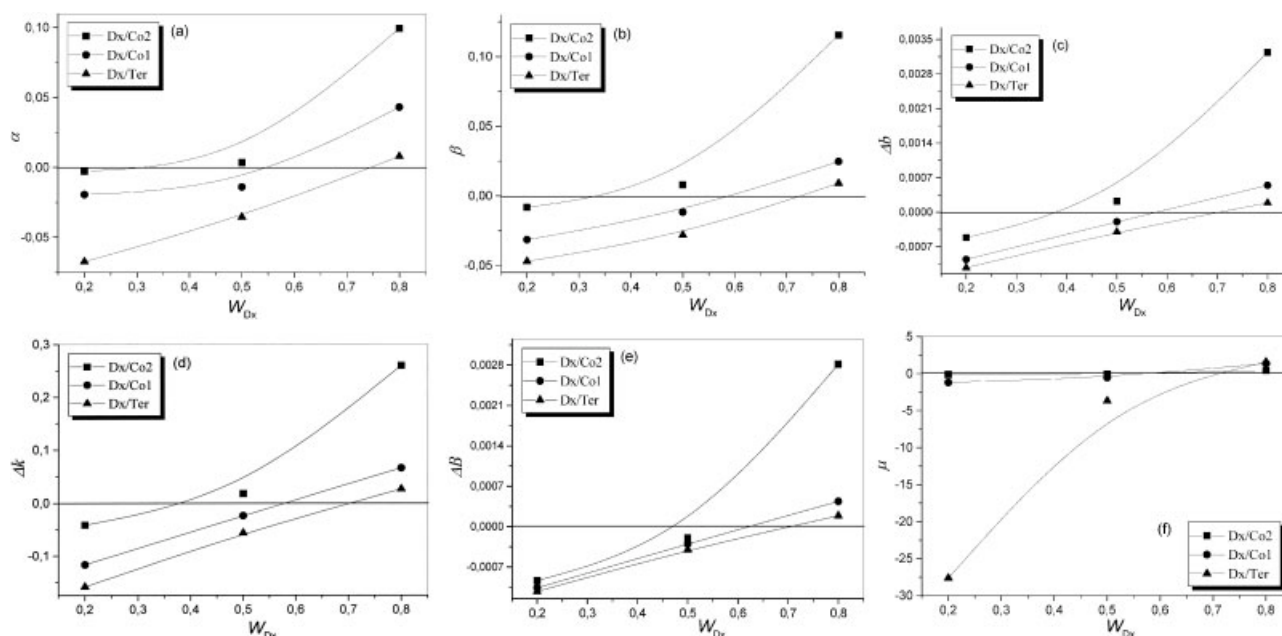


Figure 1 Concentration dependence of (a) α , (b) β , (c) Δb , (d) Δk , (e) ΔB , and (f) μ in different blend systems.

presence of atmospheric H_2O . This reversible reaction of hydrolysis of citraconic anhydride is given in Scheme 1.

In the structure of synthesized co- and terpolymers, not only the carboxylic groups of hydrolyzed CA units but also the $-NH_2$ and $-C=O$ groups of AAm units and $O-C=O$ groups of VA units were present as functional sites. Given the structure of Dx, it was strongly expected that its functionality also was a result of the $-OH$ and etheric $-O$ groups on the polymer backbone.

Vasile et al.²⁸ investigated the miscibility of Dx with maleic acid-vinyl acetate (MAc-VA) copolymer and found the same results as ours (high miscibility at high amounts of Dx). Also, they found significant evidence of the formation of chemical bonds between the $-COOH$ groups of the MAc-VA copolymer and the primary $-OH$ groups of Dx by using spectroscopic and thermal analysis methods. It easily could be expected that the same interactions would occur between the $-OH$ groups of Dx and the functional groups of related copolymers (especially, $-COOH$ groups from hydrolyzed citraconic anhydride and $-NH_2$ groups from acrylamide). The possible interactions between the polymer segments can be presented in the following form shown in Scheme 2.

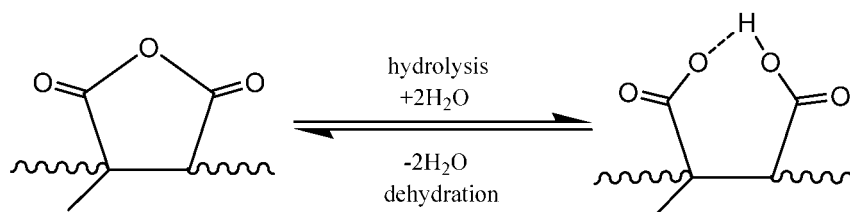
As can be seen in Scheme 2, a polymeric blend system might have two types of interactions between the polymer molecules: (1) intra- and intersegmental interactions between the same polymers and (2) intersegmental interactions between the different polymers. Competition between the first and second types of interactions was strongly expected to occur. In other words, when the first type of interaction increased, the second would decrease and vice versa. It is generally known that polymer-polymer miscibility is enhanced by specific interactions between the different polymer segments. Thus, the second type of interaction increased miscibility, whereas the first decreased it.

Given the structures of the polymers studied, it could be easily seen that the synthesized binary and ternary copolymers had greater functionality than Dx. Thus, although H-bonds would be established between the copolymers and Dx for the chains of synthesized copolymers, the first type of interaction (interactions with a chain of its own kind) was more

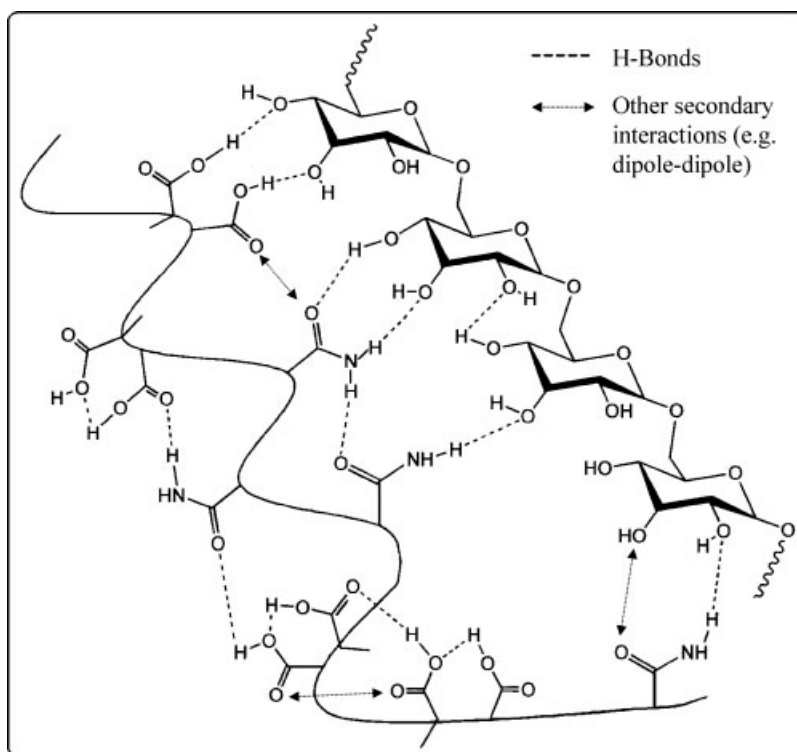
favorable than the second type (interaction with a Dx segment). As the weight fraction of the copolymers in the blends increased, establishment of any interaction with a chain of their own kind became more probable. In other words, the first type of interaction between the copolymer segments, which was already favorable, became much more dominant. This increase resulted in a decrease in the incidence of the second type of interaction because of the competition between them. Consequently, with a low weight fraction of Dx, immiscibility was observed between Dx and related copolymers, as can be seen in Figure 1(a-f).

When two polymers are blended, there is always a trace of one in the other, and for most polymer pairs this solubility limit is very low and polymers are classified as immiscible. It has been found that for a greater number of polymer mixtures than was previously suspected, regions of miscibility may exist.²⁹ This means that, although miscibility was observed only with high amounts of Dx according to the experimental results, it was strongly expected that when a small amount of Dx was added to the synthesized copolymer samples, a part of copolymer would be miscible with Dx. When the amount of added Dx was increased, the probability of establishment of less favorable interactions between Dx and related copolymers also increased because the Dx chains became more available for bonding, and hence, a trend that enhanced miscibility was observed with increasing Dx content, as can be seen from Figure 1(a-f). After a critical concentration was reached, the unfavorable interactions between Dx and copolymer overcame the interactions between the copolymer segments. In other words, the limit on solubility was destroyed; consequently, miscibility was observed with high weight fractions of Dx, as the experimental results showed.

In Figure 1(a-f) it can be easily seen that the miscibility of blend samples increased not only with the weight fraction of Dx but also with an increasing amount of AAm unit in the copolymer composition. For all the miscibility parameters except μ , all compositions of the Dx/Co2 blend system showed higher miscibility than the other two blend systems. The major difference between the Co1 and Co2 copolymer samples was their AAm content. The Co2 co-



Scheme 1 Reversible hydrolysis equilibrium of citraconic anhydride.



Scheme 2 Possible interactions for the blend system.

polymer sample had a larger amount of AAm than Co1. Given the difference in the miscibility behavior of Co1 and Co2 with Dx, it would be expected that the first type of interaction would be more favorable for the $-\text{NH}_2$ groups of the acrylamide units than for the $-\text{COOH}$ groups of the anhydride units because the copolymer sample that contained a greater amount of acrylamide, Co2, exhibited greater miscibility. As can be seen in the hydrolysis equilibrium of CA, shown in Scheme 1, the CA units preferred intramolecular H-bonding with the $-\text{COOH}$ groups in their structure. This caused a decreased interest by the CA units in the Dx chains, and hence Co1 (the copolymer sample composed of a greater amount of CA) exhibited less miscibility than did Co2.

As can be seen in Figure 1(a–f), of the systems studied, the Dx/Ter blend sample showed the least miscibility. It is well known from theoretical and experimental studies that miscible blends result from exothermic interactions, especially those resulting from hydrogen bonding between unlike blend components.^{22,30} Using this definition, it is not surprising that the Dx/Ter system showed the least miscibility because the H-bonding capability of the VA units would be expected to be less than that of the CA and AAm units because VA has no hydrogen atom bonded to a strongly electronegative atom (e.g., O or N) in its structure. The addition of VA to a copolymer decreased the quantity of CA and AAm units in the copolymer. Consequently, for the terpolymer

sample [poly(CA-co-AAm-co-VA)], it became less likely that interactions such as H-bonds would occur with Dx chains. Hence, the Dx/Ter system exhibited the least miscibility.

FTIR analysis

Characterization of specific bands obtained by FTIR spectral analysis can be found in our previous studies for the synthesized copolymers²⁴ and Dx.²⁰ To investigate the interactions that occurred between Dx and related copolymers when they were blended, comparing the differences between the experimentally measured FTIR spectra and the computationally calculated data is a good method because the experimental spectra show the actual interactions, whereas the computational ones are only for mechanical mixtures of two polymers. One region of the FTIR spectra of particular interest for the polymers studied is presented in Figure 2. This region contained vibrations sensitive to interactions such as H-bonding; $-\text{O}-\text{H}$ bending and $-\text{C}-\text{O}$ stretching vibrations of Dx; and $-\text{C}=\text{O}$ stretching, $-\text{N}-\text{H}$ bending, and $-\text{C}-\text{O}$ stretching vibrations of synthesized copolymers.^{20,24} The computational spectra shown in Figure 2 were calculated by adding the appropriate fractions (by mass) of the pure Dx and copolymer spectra as given in the literature.³¹ From Figure 2, it can be easily seen that there were significant differences between the experimental and calculated

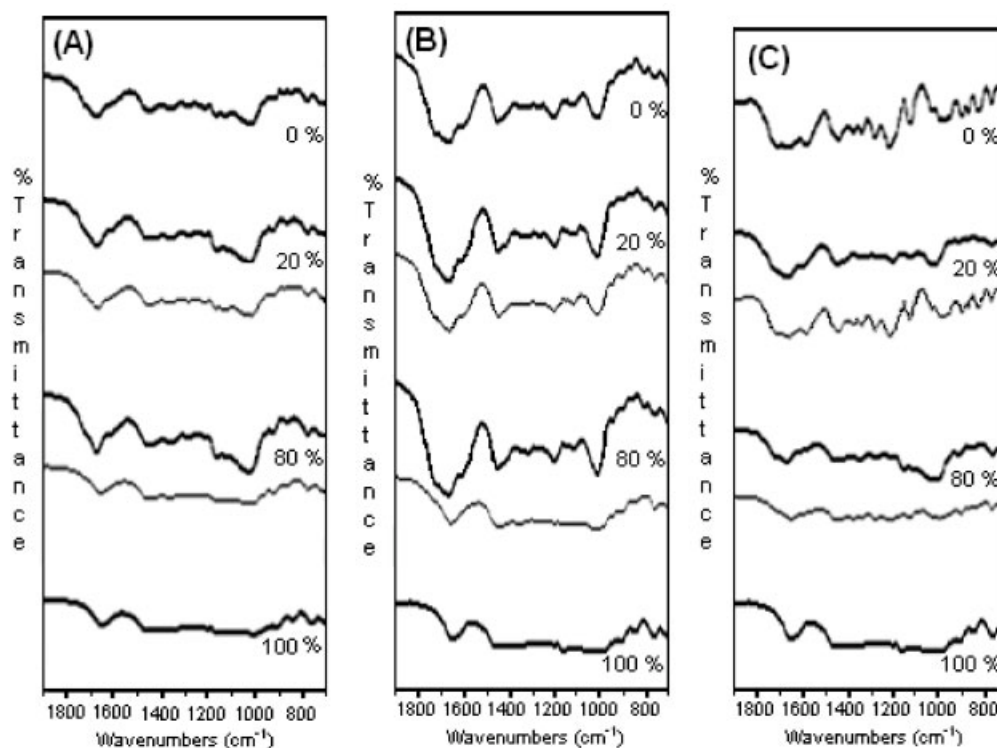


Figure 2 IR spectra of the blends (A) Dx/Co1, (B) Dx/Co₂, and (C) Dx/Ter. The lower of each pair (thinner line) was calculated from the measured spectra for pure Dx and the related copolymer, and the upper of each pair was the measured spectrum for that blend. Percentages refer to the amount of Dx in each blend.

spectra. This shows there would be some interactions when Dx and related copolymers were blended, such as those presented in Scheme 2, and that these interactions might cause partial miscibility, which was supported by the results of the viscometry.

Askadskii's solubility criterion

Experimental testing of Askadskii's criterion was performed on an example of an approximately 300 system of the polymer-solvent type.³² We employed this criterion in order to do a theoretical analysis of the miscibility between Dx and related anhydride-containing copolymers. The initial characteristics necessary for the estimation of the physical characteristics of synthesized copolymers were calculated for the repeat units of the synthesized copolymers using the above-mentioned formulas, and the results are given in Table III. The values of ΔE_i^* and ΔV_i necessary for these calculations were taken from Askadskii²² for the interactions and atoms of the systems studied. The copolymer compositions that occurred from elemental analysis and the values for cohesive energy and van der Waals volume of the repeat units, which are presented in Table III, were used to calculate the physical characteristics of the synthesized copolymers, which are given in Table IV.

To investigate the miscibility behavior of Dx and the synthesized copolymers theoretically, first it was supposed that Dx was the solvent for the Co1 copolymer sample, meaning small quantities of Co1 added to Dx.

Substituting the values of the characteristics of Dx and Co1, which are given in Table IV, into Askadskii's miscibility criterion, we obtained $0.7602 < 1.1482$.

Hence, the left-hand side of the miscibility criterion was smaller than the right-hand side, indicating Co1 would not "dissolve" well in Dx. In other words, empirically these two polymers would be expected to be miscible with each other at high contents of Dx. This theoretical result confirmed the experimental observations.

TABLE III
Initial Data for Calculation of Physical Characteristics of Synthesized Copolymers

Physical characteristics	CA	AAM	VA
Cohesive energy, $\Sigma_i \Delta E_i^*$ (J/mol)	61028.4	59950.4	41587.7
van der Waals volume, $\Sigma_i \Delta V_i$ (\AA^3)	86	64.3	79.6
Solubility parameter, δ [$(\text{J}/\text{cm}^3)^{1/2}$]	34.32	39.34	29.45
Surface energy, γ (dyn/cm)	65.12	82.53	46.73
Molar volume, V (cm^3/mol)	76.06	56.87	70.40

TABLE IV
Physical Characteristics of Dx and Synthesized Copolymers

Physical characteristics	Dx	Co1 (CA : AAm) (0.4586 : 0.5414)	Co2 (CA : AAm) (0.3004 : 0.6996)	Ter (CA : AAm : VA) (0.5834 : 0.12 : 0.2965)
Cohesive energy, $\Sigma_i \Delta E_i^*$ (J/mol)	81623.7	60444.9	60273.8	55128.8
van der Waals volume, $\Sigma_i \Delta V_i$ (\AA^3)	131.97	74.254	70.81	81.49
Solubility parameter, δ [$(\text{J}/\text{cm}^3)^{1/2}$]	32.05	36.76	37.59	33.51
Surface energy, γ (dyn/cm)	54.33	73.41	76.31	61.39
Molar volume, V (cm^3/mol)	116.72	65.67	62.63	72.07

Next, we supposed that small quantities of Dx were added to Co1. Then, using Askadskii's miscibility criterion, we calculated $1.3155 < 1.0936$

Because the left-hand side of the criterion was not smaller than the right-hand side, Dx and Co1 would not be expected to be miscible with each other at high contents of Co1 (with the addition of Dx to Co1). This theoretical result also confirmed the experimental results.

The values of the left- and right-hand sides of Askadskii's miscibility criterion were calculated in the same way for the addition of Dx to Co1, to Co2, and to Ter and vice versa. As can be seen from the results given in Table V, theoretically, miscibility would be expected with high amounts of Dx, whereas immiscibility would be expected with high amounts of Co2. In other words, the theoretical results showed that miscibility increases with the Dx content of the blend. There was good agreement between the results of the theoretical calculations and the experimental observations.

The only difference between the theoretical and experimental results was observed for the Dx/Ter blend system with a high concentration of Ter [poly(CA-co-AAm-co-VA)]: theoretically miscibility was expected, but experimentally immiscibility was observed using viscometry (Table V). However, the theoretical results still provided some important hints of support for the experimental results for this system. According to Askadskii's miscibility criterion, miscibility is indicated when the left-hand side of the criterion is smaller than the right-hand side. Thus, for the same system it may be said that as the absolute value of the difference between the left (L) and right (R) sides of the criterion ($|L - R|$) increases,

greater miscibility would be expected. As can be seen in Table V, for the Dx/Ter system the $|L - R|$ obtained for the addition of Ter to Dx was greater than the $|L - R|$ obtained for the addition of Dx to Ter ($|0.915 - 1.259| > |1.093 - 1.237|$). Thus, theoretically, greater miscibility should be expected with a large amount of Dx. In other words, the theoretical calculations for the Dx/Ter system also indicated an increase in miscibility with an increasing amount of Dx, which was in good agreement with the experimental observations.

CONCLUSIONS

In this study, miscibility between two commercially important polymers—Dx and synthesized citraconic anhydride-containing copolymers of different compositions—was investigated experimentally and theoretically. From our experimental observations it was clear that miscibility between the polymer pairs increased with an increasing amount of Dx in the blend. This behavior was consistent with the presence of functional sites in the structures of the polymers studied. It was found that the AAm units had greater interest in the Dx chains than did the CA units because of the reversible hydrolysis equilibrium of CA. Also, it was seen that the addition of VA to the copolymer caused decreased miscibility because the VA units had the least H-bonding capability among the repeat units of the synthesized copolymers. Using these experimental observations, we determined an order for the interest of the repeat units of the synthesized copolymers in the Dx chains as: AAm > CA > VA. Furthermore, we observed the experimental results for all the miscibility param-

TABLE V
Results of Application of Askadskii's Miscibility Criterion

Blend system	Probable addition	Left-hand side of criterion (L)	Right-hand side of criterion (R)	Miscibility
Dx/Co1	Co1 is added to Dx	0.7602	1.1482	Miscible
	Dx is added to Co1	1.3155	1.0936	Immiscible
Dx/Co2	Co2 is added to Dx	0.7270	1.1244	Miscible
	Dx is added to Co2	1.3756	1.0574	Immiscible
Dx/Ter	Ter is added to Dx	0.9148	1.2590	Miscible
	Dx is added to Ter	1.0932	1.2368	Miscible

ters except μ agreed with each other in predicting polymer miscibility, and FTIR analysis provided important hints about the interactions between the polymer pairs.

A theoretical investigation of miscibility also indicated that the miscibility of the studied blend systems increased with an increasing weight fraction of Dx. Thus, it may be concluded that Askadskii's miscibility criterion can be used with good agreement with experimental results to determine the miscibility/compatibility of polymer pairs. It is known that thermal and spectral methods are very valuable for investigating the miscibility/compatibility of polymer pairs. In the future, we expect to present a complementary work to this study that will contain the results of thermal and spectral analyses.

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