

Specific Interactions in Poly(styrene-*co*-2-Hydroxyethyl acrylate)/Poly(styrene-*co*-*N,N*-dimethylacrylamide) Systems

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Received 26 January 2008; accepted 28 June 2008

DOI 10.1002/app.28905

Published online 15 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Amphiphilic copolymers of poly(styrene-*co*-2-hydroxyethyl acrylate) (SHEA) and poly(styrene-*co*-*N,N*-dimethylacrylamide) (SAD) of different compositions were prepared by free radical copolymerization and characterized by different techniques. Depending on the nature of the solvent and the densities of interacting species incorporated within the polystyrene matrices, novel materials as blends or interpolymer complexes with properties different from those of their constituents were elaborated when these copolymers are mixed together. The specific interpolymer interactions of hydrogen bonding type and the phase behavior of the elaborated materials were investigated by differential scanning calorimetry (DSC) and Fourier transform infra red spectroscopy (FTIR). The specific interactions

of hydrogen bonding type that occurred within the SHEA and within their blends with the SAD were evidenced by FTIR qualitatively by the appearance of a new band at 1626 cm^{-1} and quantitatively using appropriate spectral curve fitting in the carbonyl and amide regions. The variation of the glass transition temperature with the blend composition behaved differently with the densities of interacting species. The thermal degradation behavior of the materials was studied by thermogravimetry. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3574–3581, 2008

Key words: poly(styrene-*co*-2-hydroxyethyl acrylate); poly(styrene-*co*-*N,N*-dimethyl acrylamide); interpolymer complexes; specific interactions; FTIR; DSC

INTRODUCTION

Poly(2-hydroxyethyl acrylate) is an acrylic polymer that behaves as a rubber at room temperature. Because of its high capacity of water uptake, it may form hydrogels with good biological acceptance. Although the tendency of this polymer to replace poly(2-hydroxyethyl methacrylate) has been reported in many instances, particularly to simulate the mechanical properties of soft tissues without losing its water sorption capacity,¹ the mechanical properties of this polymer are rather poor and need however to be improved.

Khutoryanski and coworkers² have synthesized amphiphilic copolymers based on 2-hydroxyethyl acrylate and vinyl butyl ether and studied their interactions with poly(carboxylic acids). Hybrid networks have been previously prepared from hydrophobic polymers such as polystyrene.³ Rodriguez Hernandez et al.⁴ have recently reported the preparation of poly(2-hydroxyethyl acrylate)-silica nanocomposites by sol-gel process that led to a hybrid material with improved mechanical properties.

Although Hydrogels made of single polymers have been used in various applications particularly in drug delivery, it is rather rare for a single polymer to satisfy simultaneously the desired properties, cost, and performance. Because blending is a simple method expected to lead to combined properties of polymers of different nature, different kinds of heterogeneous hydrogels have been investigated.⁵

Among the various hydrogel networks that may be elaborated, physical hydrogels are networks formed by physical interactions involving low energy. Such materials can be prepared by complexation through specific interactions of hydrogen bonding type between polymeric chains without addition of any crosslinkers.

It is well known that depending on the nature of solvent used, polymer complexes are formed only when polymer-polymer interactions that occurred between the components of the mixture are stronger than polymer-solvent interactions and exceed a certain level. Such strong hydrogen bonding interactions between polymers are expected to increase the thermal stability of the resulting material.

Poly(*N,N*-dimethylacrylamide) is a typical proton acceptor polymer that formed interpolymer complexes through hydrogen bonding with poly(2-hydroxypropyl methacrylate)⁶ and other polymers

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containing proton donating groups such as poly(2-hydroxyethyl methacrylate), poly(hydroxyether of bisphenol-A), poly(styrene-*co*-allyl alcohol), and poly(mono *n*-alkyl itaconate).^{7,8}

We have in a previous study⁹ reported the miscibility and complexation behaviors of PDMA and its styrene copolymers with different poly(styrene-*co*-acrylic acid). It is of interest to investigate whether PDMA and these basic copolymers can form interpolymer complexes with poly(styrene-*co*-2-hydroxyethyl acrylate). We have then in the first step of the present contribution prepared and characterized two types of copolymers of different compositions of styrene with 2-hydroxyethyl acrylate (SHEA) and with *N,N*-dimethylacrylamide (SAD). In the second step of this work, the specific interactions that occurred between the SHEA and the SAD copolymers and the miscibility and complexation behaviors were investigated by DSC and FTIR qualitatively and quantitatively. A thermal stability study of the synthesized copolymers and of their different mixtures was carried by TGA.

EXPERIMENTAL

Synthesis and characterizations

Poly(styrene-*co*-2-hydroxyethyl acrylate) containing 16, 27, and 33 mol % of 2-hydroxyethyl acrylate (SHEA-16, SHEA-27, and SHEA-33) and poly(styrene-*co*-*N,N*-dimethylacrylamide) containing 12, 18, and 24 mol % of *N,N*-dimethylacrylamide (SAD-12, SAD-18, and SAD-24) and poly(*N,N*-dimethylacrylamide) (PDMA) were prepared by free radical polymerization at 60°C in dioxane solution using azobisisobutyronitrile (AIBN) as the initiator keeping the conversion low to avoid drift composition.

The copolymers, isolated by precipitation in a non-solvent, were then purified by repeated dissolution/precipitation and dried in a vacuum oven at 60°C for several days. The composition of these copolymers was determined by elemental analysis (EA) and UV spectroscopy to determine the styrene contents.

The average molecular weights of the copolymers were determined in DMF solution by size exclusion chromatography using a Waters 2414 chromatograph equipped with refractive index detector. The comonomer compositions and the average molecular weights are listed in Table I.

Thermal analysis

Films of the various copolymers and of their blends of different ratios were prepared from chloroform solutions. These films were dried to constant weight in a vacuum oven at 60°C during several days to remove traces of solvent and used in the thermal analysis.

TABLE I
Characteristics of the Different Copolymers

	UV HEA (mol %)	EA AD (mol %)	GPC		$I = M_w/M_n$
			M_w (g/mol)	M_n (g/mol)	
SHEA-16	16		5,54,841	2,51,620	2.21
SHEA-27	27		8,18,469	3,46,616	2.36
SHEA-33	33		2,100,884	5,87,302	3.58
SAD-12		12	3,10,861	1,71,389	1.81
SAD-18		18	4,58,016	2,53,617	1.80
SAD-24		24	3,17,817	1,84,296	1.72

A DSC Q100 TA instrument differential scanning calorimeter was used to measure the glass transition temperatures T_g of these copolymers and of their blends under a nitrogen atmosphere in the 0 to 180°C temperature range. The scanning rate was of 20°C/min. The T_g is taken from the second scan as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines.

TGA thermograms of the as-cast films of the synthesized copolymers and of the SHEA-33/SAD-24 blends of different ratios were determined prior to DSC analysis using a TGA Q500 TA instrument under nitrogen atmosphere from 40 to 600°C at a heating rate of 10°C/min.

FTIR measurements

Thin films of these copolymers and of their blends of different ratios were prepared by casting from a 3% w/v solution in chloroform onto KBr disks. The films were kept in a vacuum oven for several days at 60°C until the solvent was removed. The FTIR spectra were recorded at room temperature with a BIORAD EXCALLIBUR FTIR spectrometer using 60 scans at a resolution of 2 cm⁻¹.

RESULTS AND DISCUSSION

When chloroform or THF solutions of SHEA-33 and SAD-24 copolymers were mixed together, homogeneous phases were observed. Similar observations were noted with mixtures formed of copolymers containing lower densities of interacting species. Interpolymer complexes were however observed with SHEA-27 or SHEA-33 and PDMA when butanone was the common solvent.

Thermogravimetric analysis

SHEA copolymers

This thermogravimetric analysis showed that these copolymers were stable up to 450°C as displayed from their TGA and first derivative d(TGA) curves

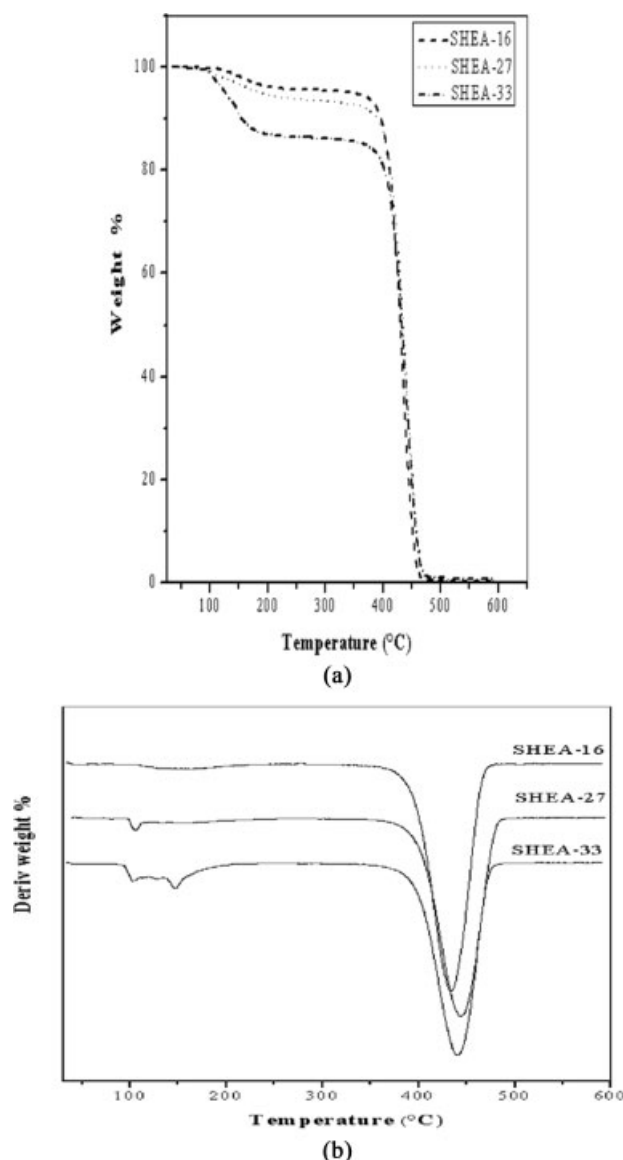


Figure 1 (a) TGA curves of the SHEA copolymers. (b) d(TGA) curves of the SHEA copolymers.

Figure 1(a,b) Two steps of degradation were observed with these copolymers. The first step is attributed to loss of adsorbed water (Δm %) which was found as expected to increase with the hydrophilicity of the copolymer. The second step corresponds to the main degradation of the component whose temperature of maximum degradation

increases with HEA content for the SHEA copolymers. This thermal stability is mainly due to an increase of self (hydroxyl-carbonyl and hydroxyl-hydroxyl) associations within the SHEA copolymers. The thermogravimetric parameters of these copolymers are shown in Table II.

SHEA-33/SAD-24 blends

The thermogravimetric traces (TGA) of SHEA-33, SAD-24, and their blends of different ratios and of their corresponding derivative thermogravimetric d(TGA) are shown in Figure 2(a,b) while Table III summarizes their thermogravimetric parameters that also includes among others the temperatures at which 5 and 50% degradation occurs. It is evident from these figures that the thermal degradation of SHEA-33/SAD-24 blends proceeds by two steps processes, which is represented by two peaks in the corresponding d(TGA) curves. The first step, located between 92 and 208°C is attributed to loss of adsorbed water (The HEA and AD comonomers have hydrophilic characters), the second step corresponds to the degradation of the blend, whose temperature of maximum degradation increases with SHEA-33 composition increase in the SHEA-33/SAD-24 blends.

These results show that the thermal stability of the as-cast SAD-24 matrix decreases upon addition of SHEA-33 though this latter has a higher stability. The observation of one step of degradation in the second stage is an evidence of the formation of a single phase although a negative deviation of the T_{\max} of the blend with the composition is observed. Besides the decrease of the self-associations that occurred within the SHEA copolymer, on mixing it with the SAD copolymer and that will be evidenced below by FTIR spectroscopy, the TGA curves of the as-cast components and their blends displayed the presence of adsorbed water of different strength that inhibited the interpolymer interactions of hydrogen bonding type that would have enhanced the thermal stability. Yet these specific interpolymer interactions that occurred between the hydroxyl groups of the SHEA-33 and the amide groups of SAD-24 contribute to a water retention decrease by the blends compared to the pure copolymers.

TABLE II
Thermogravimetric Parameters of SHEA Copolymers

	$\Delta T(^{\circ}\text{C})$ (Step 1)	$\Delta T(^{\circ}\text{C})$ (Step 2)	$T_{\max 1}$ ($^{\circ}\text{C}$)	$T_{\max 2}$ ($^{\circ}\text{C}$)	$T_{5\%}$ ($^{\circ}\text{C}$)	$T_{50\%}$ ($^{\circ}\text{C}$)	% Δm (H_2O)
SHEA-16	112–219	333–473	148	434	307	430	4
SHEA-27	95–218	343–478	102	439	172	434	6
SHEA-33	94–197	350–487	102–145	440	124	435	13

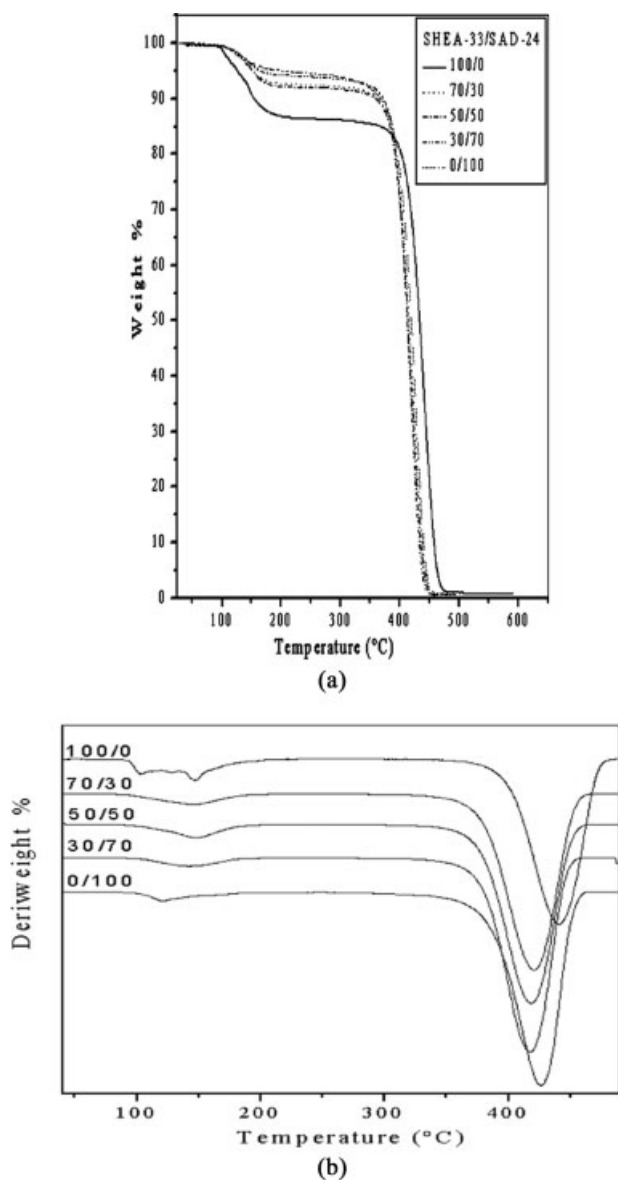


Figure 2 (a) TGA curves of SHEA-33, SAD-24, and of their blends of different ratios. (b) d (TGA) curves of SHEA-33, SAD-24, and of their blends of different ratios.

Thermal analysis

A DSC analysis was carried out for the solid state SHEA-16/SAD-24, SHEA-27/SAD-24, and SHEA-

33/SAD-24 binary blends and of SHEA-27/PDMA cast from chloroform solutions or SHEA-33/PDMA complexes. Figure 3 illustrates as an example the thermograms of the copolymers SHEA-27 and SAD-24 and of their corresponding binary blends of different ratios. The single glass transition temperature observed with each blend of the different binary systems is an evidence of their miscibility.

Figure 4 shows the T_g -composition curves for the SHEA-16/SAD-24 and SHEA-33/SAD-24 binary blends. Different behaviors were observed.

For the SHEA-33/SAD-24, the T_g values are higher than those calculated by the additivity rule and the curve is fitted by the Kwei equation given by:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2 \quad (1)$$

where w_i and T_{gi} are the weight fractions of the components and T_{gi} their corresponding glass transition temperature.

Indeed as reported by Coleman and coworkers¹⁰ and Katime and coworkers,¹¹ the Kwei constant depends on both processes of self-association and interassociation in the blend.

The q constant estimated from the equation above for this system is 23. This indicates that stronger interactions occurred between the SHEA-33 and the SAD-24.

As the HEA content decreased to 16 mol %, a negative deviation is observed in the whole composition range. The q parameter, determined by the fitting of Kwei eq. (1), has a negative value ($q = -10$). The similar behavior is observed by Katime and coworkers,¹² for the poly(vinyl acetate-co-vinyl alcohol)/poly(*N,N*-dimethylacrylamide) systems.

As mentioned above, the T_g -composition behavior varied with the densities of interacting species. Indeed while an S shaped T_g -composition is observed for the SHEA-27/SAD-24 blends cast from chloroform. The system SHEA-27/PDMA cast from the same solvent displayed a positive deviation, fitted by the Kwei equation above ($q = 39$) confirms the presence of stronger and denser interpolymer interactions that occurred within this system, due to the higher number of basic sites with PDMA

TABLE III
Thermogravimetric Parameters of SHEA-33, SAD-24, and their Blends

Wt %	ΔT (°C) (step 1)	ΔT (°C) (step 2)	T_{max1} (°C)	T_{max2} (°C)	T5% (°C)	T50% (°C)	% Δm (H ₂ O)
0/100	96–208	288–458	121	426	169	418	5
10/90	108–198	245–446	151	412	162	407	6
30/70	104–187	298–450	142	417	158	411	6
50/50	98–192	298–456	148	418	150	413	8
70/30	97–192	306–458	147	421	149	415	7
90/10	92–183	310–457	141	423	148	418	6
100/0	94–197	350–487	102–145	440	124	435	13

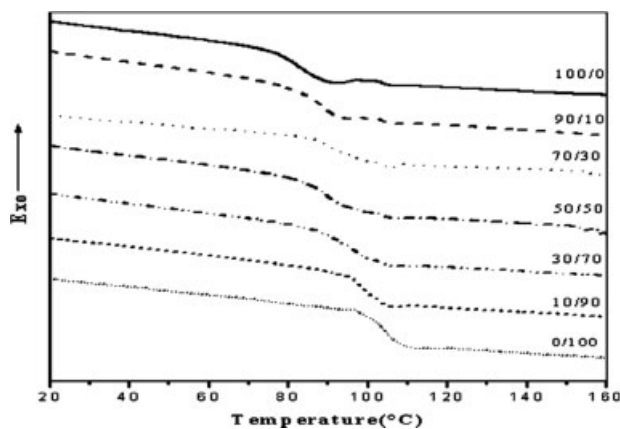


Figure 3 Thermograms of SHEA-27, SAD-24, and of their blends of different compositions.

compared to SAD-24 copolymer. Figure 5 illustrates the glass transition temperature dependence with the blend composition for the SHEA-27/SAD-24 and SHEA-27/PDMA blends.

FTIR analysis

Self association within the SHEA copolymers

Figure 6 depicts the scale expanded infrared spectra of the SHEA copolymers recorded at room temperature in the hydroxyl region. The spectrum of SHEA-33 shows in this hydroxyl 3750–3100 cm^{-1} region, a shoulder at 3580 cm^{-1} attributed to free hydroxyl groups and a broad band centered at 3478 cm^{-1} , due to the overlapped hydrogen bonded hydroxyl groups with carbonyl groups and with other hydroxyl groups (Scheme 1).

SHEA copolymers containing lower HEA contents showed two similar bands, both shifting slightly to higher wave numbers. This is an evidence of a slight decrease of the intensity of interactions with a decrease of HEA content. Katime and coworkers¹³

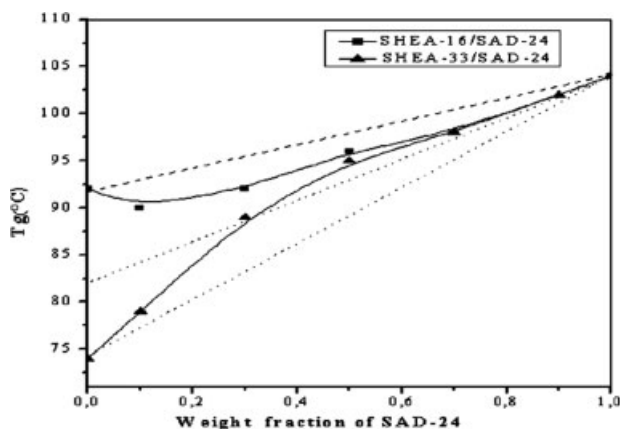


Figure 4 Glass transition temperature dependence with blend compositions of SHEA-16/SAD-24 and SHEA-33/SAD-24 blends.

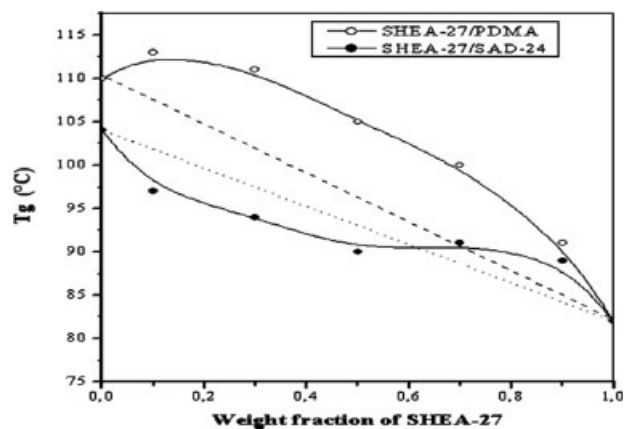


Figure 5 Glass transition temperature dependence with blend compositions of SHEA-27/PDMA and SHEA-27/SAD-24 blends.

observed a broad band centered at 3370 cm^{-1} and a shoulder at 3524 cm^{-1} for pure poly(2-hydroxyethyl methacrylate).

Because of the dilution effect with styrene moieties, the value of the estimated average strength between the hydrogen-bonded hydroxyl absorption and free hydroxyl absorption for the SHEA-33 copolymer of 102 cm^{-1} is found to be much lower and therefore weaker compared to the one of the pure poly(2-hydroxyethyl methacrylate) (154 cm^{-1}).

Besides, two bands are detected in the carbonyl region for these copolymers. A free carbonyl band around 1732 cm^{-1} and a carbonyl hydrogen bonded with the hydroxyl groups appearing as a significant shoulder at 1712 cm^{-1} . The intensity of this latter band increased with an increase of HEA content within the copolymers (Fig. 7).

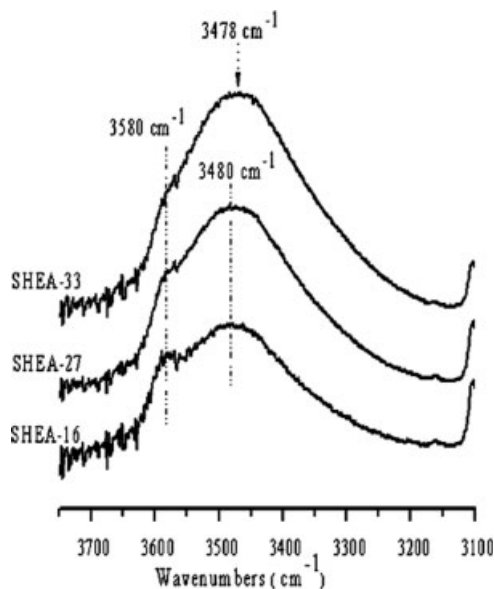
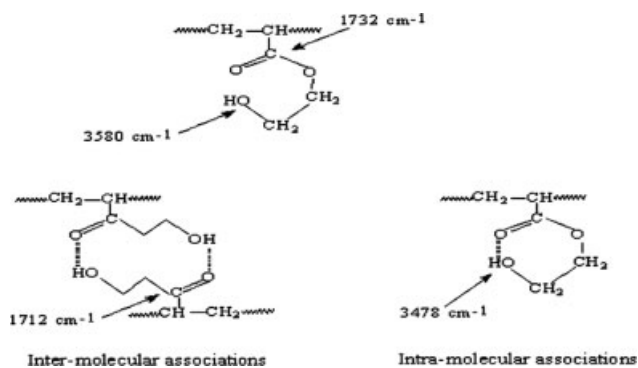


Figure 6 Scale-expanded infrared spectra of SHEA copolymers in the hydroxyl region.



Scheme 1 Self association within the SHEA copolymers.

The evolution of the fraction of free and associated carbonyl-ester groups as the 2-hydroxyethyl acrylate content varies in the SHEA copolymers.

We calculated the fraction of free carbonyl-ester F_F from the equation below using an adequate curve fitting procedure carried out in the 1780–1680 cm^{-1} carbonyl stretching region:

$$F_F = \frac{A_F}{A_F + A_A/a} \quad (2)$$

where A_F and A_A are the areas under the peaks of free and associated carbonyl groups respectively and a the ratio of the molar absorption coefficients taken as 1.23.⁶

Table IV summarizes the calculated results for the copolymers under study.

The obtained results summarized in Table IV agree with our previous qualitative study. The percentage of free carbonyl-ester groups in the SHEA copolymers diminishes as the content of HEA monomers increases.

SHEA-33/SAD-24 blends

For illustration, Figure 8 displays FTIR spectra of SHEA-33 and its blends of different ratios with SAD-24 in the hydroxyl region. As it can be seen, the center of the main broad band initially observed at 3478 cm^{-1} with SHEA-33, shifts gradually to lower wavenumbers as the SAD-24 content in the blend increases. The average strength of hydrogen bonding was measured from the frequency difference ($\Delta\gamma$)

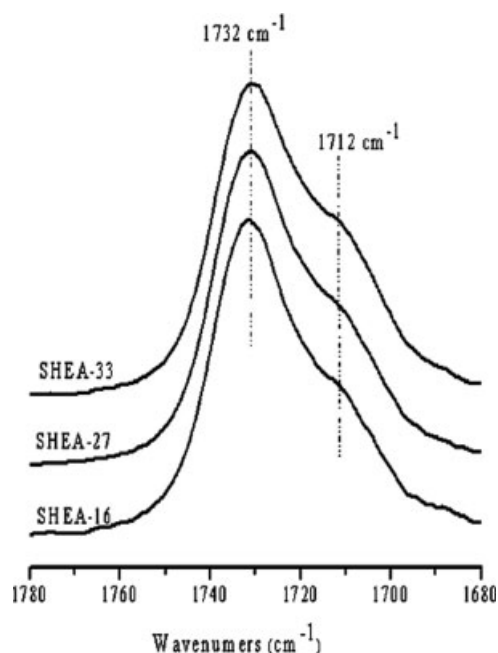


Figure 7 Scale-expanded infrared spectra of SHEA copolymers in the carbonyl region.

between the free hydroxyl groups and those hydrogen bonded. The results confirm that the interactions that occurred between the hydroxyl groups and the carbonyl amide are stronger than those between the hydroxyl and the ester carbonyl groups in the SHEA.

Indeed as the SAD content in the blend increases, the main peak at 3478 cm^{-1} shifts gradually to 3430 cm^{-1} . The frequency shift of the maximum of the 50/50 blend is 150 cm^{-1} higher than the one corresponding to the interactions within the pure SHEA-33 of about 102 cm^{-1} (Scheme 2).

These results are evidenced qualitatively in the 1780–1560 cm^{-1} region. Figure 9 illustrates the FTIR spectra of SHEA-33, SAD-24 and their different blends recorded at room temperature in this region. SAD-24 has a strong absorption at 1645 cm^{-1} assigned to the free carbonyl band of the amide. A new band appeared at 1626 cm^{-1} upon mixing SAD-24 with SHEA-33. This latter band is attributed to the hydroxyl-carbonyl amide interactions. The decrease of the intensity of the hydrogen bonded carbonyl band, observed at 1712 cm^{-1} with an

TABLE IV
Curve-Fitting Results of the Carbonyl-Ester Band in the SHEA Copolymers

	Free carbonyl ester band			H-Bonded carbonyl ester band		
	Wave number (cm^{-1})	Width (cm^{-1})	F_F	Wave number (cm^{-1})	Width (cm^{-1})	F_A
SHEA-16	1732	19	0.73	1712	21	0.27
SHEA-27	1732	19	0.70	1712	22	0.30
SHEA-33	1732	19	0.67	1712	22	0.33

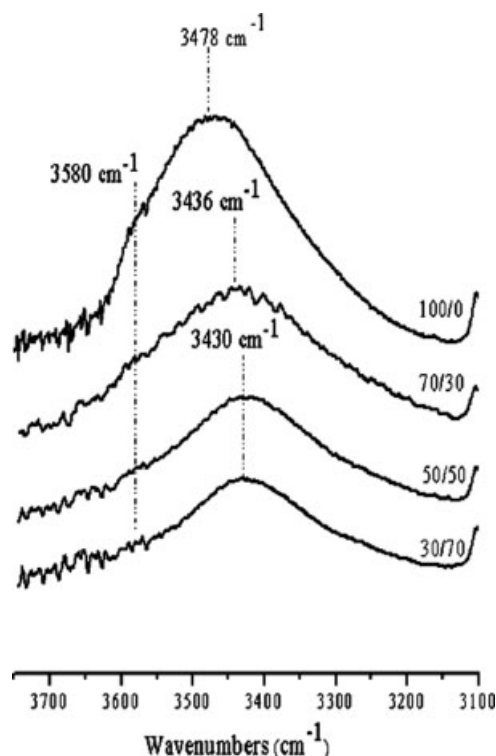
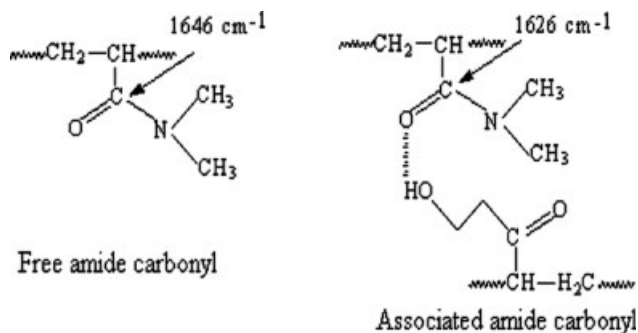


Figure 8 Scale-expanded infrared spectra of SHEA-33/SAD-24 blends in the hydroxyl region.

increase of SAD-24 content in the blends indicates a preference of hydroxyl groups of SHEA-33 to interact with the amide groups through stronger interactions than with the ester carbonyl groups.

A quantitative analysis using adequate curve fitting procedure was carried in the 1780–1680 cm^{-1} carbonyl stretching region to determine the evolution of the fraction of free and associated carbonyl groups of SHEA-33 as the SAD-24 content is added within the blends using a Gaussian function. The fraction of free carbonyl F_F was determined from eq. (2).

The results summarized in Table V show that the fraction of free carbonyl groups increases with SAD-24 content in the blend.



Scheme 2 Free amide carbonyl and hydroxyl-amide inter association.

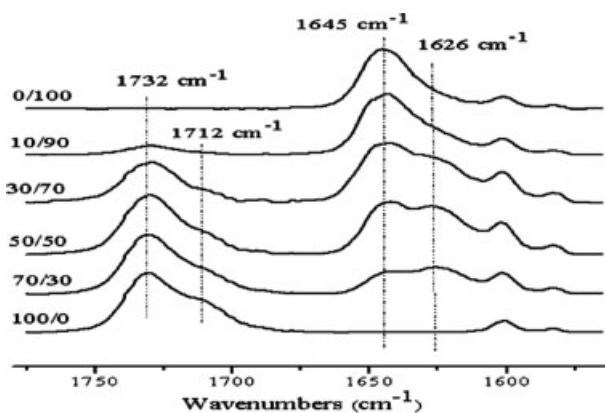


Figure 9 Scale-expanded infrared spectra of SHEA-33/SAD-24 blends in 1780–1560 cm^{-1} region.

In a similar way the fraction of hydrogen bonded carbonyl amide groups was estimated in the carbon region, using eq. (2) and an absorptivity ratio of 1.30.⁶ The results shown in Table VI indicate that the intermolecular interactions between the hydroxyl groups and the amide carbonyl groups increase with SHEA-33 amount in the blend. This quantitative analysis also confirms that stronger intermolecular interactions occurred mainly between the hydroxyl groups of SHEA-33 and the carbonyl amide groups of SAD-24. Indeed, as shown in Tables V and VI, the fractions of hydrogen bonded amide carbonyl groups are much higher than those of hydrogen bonded ester groups. These results are in agreement with those obtained by DSC.

CONCLUSIONS

This study showed that poly(styrene-*co*-2-hydroxyethyl acrylate) copolymers containing more than 27 mol % of 2-hydroxyethyl acrylate formed interpolymer complexes with PDMA in butanone but not in chloroform due to the presence of stronger intermolecular hydrogen bonding association that occurred between the amide carbonyl groups and the

TABLE V
Curve-Fitting Results of the Carbonyl-Ester Bands in the SHEA-33/SAD-24 Blends

Wt %	Free carbonyl ester band			Associated carbonyl ester		
	Wave number (cm^{-1})	Width (cm^{-1})	F_F	Wave number (cm^{-1})	Width (cm^{-1})	F_A
100/0	1732	19	0.67	1712	22	0.33
70/30	1731	19	0.73	1712	23	0.27
50/50	1730	22	0.86	1709	16	0.14
30/70	1730	23	0.93	1708	11	0.07
10/90	1730	22	0.94	1707	12	0.06

TABLE VI
Curve-Fitting Results of the Carbonyl-Amide Bands in the SHEA-33/SAD-24 Blends

Wt %	Free carbonyl amide band			Associated carbonyl amide		
	Wave number (cm ⁻¹)	Width (cm ⁻¹)	F_F	Wave number (cm ⁻¹)	Width (cm ⁻¹)	F_A
70/30	1645	18	0.40	1624	27	0.60
50/50	1646	17	0.45	1626	27	0.55
30/70	1647	19	0.50	1627	30	0.50
10/90	1646	17	0.53	1632	31	0.47
0/100	1646	18	1			

hydroxyl groups in SHEA compared to the hydroxyl-hydroxyl and hydroxyl-ester carbonyl self-association within these latter polymers as evidenced by FTIR. The DSC study confirmed in the T_g -composition analysis the crucial role of hydrogen bonding in the phase behavior of these miscible blends or interpolymer complexes as diverse equations were used to quantify the strength of these interactions. The interpolymer hydrogen bonding developed between the amide and hydroxyl groups produced stiffer materials.

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