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Interpolymer complexation and thermal behaviour of poly(styrene-*co*-maleic acid)/poly(vinyl pyrrolidone) mixtures

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ABSTRACT

Polymer complexation between poly(styrene-*co*-maleic acid), (SMA28) and (SMA50) containing 28 and 50 mol% of maleic acid and poly(vinyl pyrrolidone) (PVP), has been investigated by differential scanning calorimeter (DSC), Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). All results showed that the ideal complex composition of SMA28/PVP and SMA50/PVP leads, respectively, to 2:1 and 1:1 mole ratio of interacting components.

For the investigated systems, the T_g versus composition curve does not follow any of the usual proposed models for polymer blends. Withal, a new model proposed by Cowie et al. is used to fit the T_g data and it is found to reproduce the experimental results more closely. According to n and q obtained values, it seems reasonable to conclude that the inter-associated hydrogen bonds dominate in SMA28/PVP (2:1) complexes. This effect is corroborated by the FTIR study as evidenced by the high displacement of the specific bands and ionic interactions have been clearly identified. Finally, a thermogravimetric study shows that ionic interactions increase the thermal stability of these complexes.

1. Introduction

It is well known that intermacromolecular complexes can be obtained by mixing solutions of two complementary copolymers [1–6]. Complex formation are usually divided into four classes of specific interactions known as hydrogen-bonding [1–3], dipolar interactions [4], van der Waals forces [5] and charge transfer [6]. It is believed that gradually increasing of the density of one of the specific interaction groups in a polymeric system can form a complex that precipitates when the two constituent polymer solutions are mixed in a common solvent [7,8]. However, because of the more compact nature of complexes, the T_g values of complexes are higher than those of miscible blends of the same system with similar compositions [9,10].

The research on the intermacromolecular complexation due to hydrogen-bonding began as early as the 1960s and among the use of the proton-donating polymers, the study the complexation of poly(vinyl phenol) (PVPh) has been the most extensively employed. Pearce's group [11] took up the complexation of PVPh with a series of proton-accepting polymers including poly(*N*,*N*-dimethyl acrylamide) (PDMA), poly(ethyl oxazole) (PEOX) and poly(vinyl pyrrolidone) (PVP). Depending on the solvent used, the mixture may either precipitate as a complex or give a clear solution which can be used to obtain blend after solvent evaporation. Moreover, polymer containing piperidine groups are found to form complexes with PVPh by hydrogen-bonding formation between piperidine and hydroxyl groups. However, according to Luo et al. [12], although poly(*N*-methyl-4-piperidyl methacrylate) complexed with PVPh in ethanol over the entire feed composition as judged by precipitation and evidenced by FTIR study which stated that driving force of complexation would be the hydrogen-bonding between the carbonyl of PMPMA and the hydroxyl of PVPh. A large number of systems that form interpolymer complexes are known and have already found many potential uses, e.g., in technology [13,1] for optical applications, and medicine [14] in such areas as biosensors and drug delivery.

While miscibility and complexation studies involving different polyacid copolymer, containing cinnamic acid [15–17], *para*-carboxy styrene [18], itaconic acid [19], acrylic and methacrylic acid [20–21] monomers, have been extensively studied, the complexation of systems containing maleic acid monomer have received less attention.

We have recently reported the study of the interpolymer complexation of hydrolyzed poly(styrene-*co*-maleic anhydride) with poly(styrene-*co*-4-vinyl pyridine) [22]. The results showed that the composition of the complex obtained from different feeds,

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Table 1
Characteristics of the polymers

Polymers	Composition of MA (mol%)			$M_w \times 10^{-5}$ (g/mol)	M_w/M_n
	^{1}H NMR	Acid titration	E.A.		
SMA50	49.10	49.63	51.66	2.19	1.08
SMA28	28.51	27.52	27.98	2.09	1.32
PVP	–	–	–	0.94	1.29

approaches an ideal ratio which gives the main yield, the highest value of the T_g and the best thermal stability of the complex. The present study deals with the complexation between poly(styrene-*co*-maleic acid) and poly(vinyl pyrrolidone). The system described here consists of a strongly associated dicarboxylic polyacid (SMA) and a weekly self-associated copolymer (PVP). It is shown that these copolymers, under given experimental conditions, form complexes as a result of both hydrogen-bonding and electrostatic interactions, as evidenced by the FTIR results. Additionally the complexation of these systems were established using a new formalism developed by Cowie et al. [23,24] and based on the application of the modified Kwei equation in order to quantify the extend of the hydrogen-bonding interactions in SMA/PVP interpolymer complexes from the composition dependence of the glass transition.

2. Experimental

2.1. Materials

The synthesis of poly(styrene-*co*-maleic anhydride), copolymers containing 50 and 28 mol% of maleic anhydride (MA) content has been described previously [22]. The PVP used in this study was purchased from Fluka Chemical Company, Inc., USA. The weight-average molecular weight M_w of the used polymers were determined from THF solutions by size exclusion chromatography using polystyrene standards with Waters GPCII.

The poly(styrene-*co*-maleic anhydride)s copolymers were hydrolyzed in refluxing water–butanone (20/80, wt%) solution at 60 °C for 4 days. The solutions were then poured in excess of petroleum ether. The precipitates poly(styrene-*co*-maleic acid), SMA28 and SMA50 were dried in a vacuum oven at 65 °C for 2 weeks.

The composition of poly(styrene-*co*-maleic acid), SMA50 and SMA28 was determined by elemental analysis (E.A.) and NMR spectroscopy using the ^{1}H NMR spectra of the copolymers, recorded with a Varian 400 MHz VnmrJ.2.1A spectrometer at 400 MHz, in DMSO-d6 using tetramethyl silane (TMS) as an internal standard. Their solutions were prepared by dissolving ca. 20 mg of specific polymer in DMSO-d6 with TMS as an internal standard. Also the acid content in SMA copolymers was determined by titration of the corresponding polymer solution in benzene-methanol (20/80, v/v) with a standardized sodium hydroxide solution.

Poly(styrene-*co*-maleic anhydride)s were found to be 100% hydrolyzed according to the acid titration and the NMR results. Moreover FTIR characterization of the acid copolymers shows that the two bands of the five ring cyclic anhydride corresponding to maleic anhydride groups have almost disappeared in the hydrolyzed copolymers spectra, as it will be detailed later in the FTIR part. The main molecular characteristics of the polymers used in this work are listed in Table 1.

2.2. Preparation of interpolymer complexes

SMA28, SMA50 and PVP were separately dissolved in 1,4-dioxane (2%, w/v). The precipitates were formed immediately upon mixing the SMA and PVP solutions. After 2 days continuous stirring, polymer complexes in the form of precipitates were isolated by centrifugation and then washed with the same solvent. The precipitates were then dried in a vacuum for 2 weeks, at 65 °C, to ensure total elimination of residual solvent and stored in desiccators to prevent moisture absorption.

The yield values reported in Table 2 correspond to the ratio between the amount of dried complex and the total amount of the two polymers in the initial solution.

The nitrogen contents of the various complexes were determined by elemental analysis using a PerkinElmer 2400 elemental analyser, and the weight of the sample was about 2 mg in all cases. The bulk composition of the complexes was calculated from their nitrogen content, which is proportional to the amount of PVP.

2.3. T_g measurements

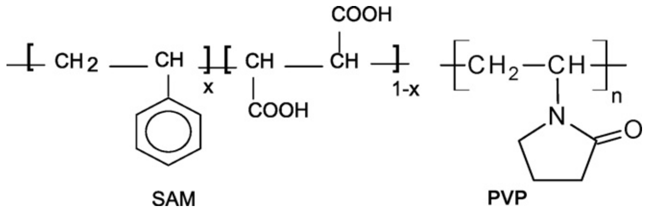
The glass transition temperatures (T_gs) of the samples were measured with a TA Instrument 2010, DSC2 differential scanning calorimeter (DSC), using a sample size of approximately 10–15 mg at a heating rate of 20 K/min, under nitrogen flow. The initial onset of the change of slope in the DSC curve is taken to be the T_g. All samples were preheated to 180 °C and kept for 10 min at that temperature to ensure complete removal of any trace of solvent. Therefore a precaution was taken not to exceed 180 °C in the first scan to avoid the formation of anhydride which can modify the structure of the initial copolymers and arise the value of the T_gs. After the thermal scan experiments, obtained T_g values were also plotted against the complexes' compositions for investigating the T_g–composition relationships.

2.4. Fourier-transform infrared spectroscopy measurements

FTIR spectra were recorded on a Bio-Rad 165 FTIR spectrophotometer. Sixty-four scans were signal-averaged at a resolution of 2 cm^{-1}. Complex samples were prepared by grinding the dry complex with KBr and compressing the mixture to form disks.

Table 2
Characteristics of SMA50/PVP and SMA28/PVP complexes

SAM50/PVP									
Weight fraction of SAM50	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
Molar fraction of SAM50	0.07	0.13	0.20	0.27	0.33	0.34	0.47	0.54	0.60
Molar fraction of SAM50 in the complex	0.16	0.24	0.36	0.44	0.57	0.68	0.78	0.84	0.93
Yield of the complex (%)	52	69	92	90	96	88	89	89	85
T_g (°C)	224	232	240	242	244	244	242	239	226
SAM28/PVP									
Weight fraction of SAM28	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
Molar fraction of SAM28	0.08	0.15	0.23	0.30	0.38	0.46	0.53	0.61	0.68
Molar fraction of SAM28 in the complex	0.24	0.47	0.56	0.67	0.72	0.75	0.80	0.85	0.93
Yield of the complex (%)	13	18	32	49	66	82	89	74	44
T_g (°C)	170	176	190	213	225	235	226	212	191



Scheme 1. Chemical structures of the polymers used in this work: poly(styrene-*co*-maleic acid) (SAM) and poly(vinyl pyrrolidone) PVP.

2.5. Thermogravimetric measurements

Thermogravimetric (TG) and differential thermogravimetric (DTG) measurements were performed using a DuPont Thermal Analyser 2000 (50 cm^3/min nitrogen flow). About 10 mg of sample was heated in a platinum crucible from ambient temperature to 600 °C, at a heating rate of 10 °C/min. The fractional conversions and their corresponding temperatures at which changes occurred were evaluated using the general analysis software version V4.0D. The onset temperature of decomposition was determined from the inflection point, by extrapolation of the initial base of the TG curves.

3. Results and discussion

3.1. Interpolymer complexation

The chemical structures of the polymers studied are given in Scheme 1. The SMA50 and SMA28 samples form insoluble complexes with PVP in 1,4-dioxane solutions, within the entire feed composition. The formation of complexes is guided by the interaction between the two polymers, and the solvent. If the former is stronger than the latter, an interpolymer complex is formed. The formation of precipitates in these systems is generally attributed to the co-operative hydrogen-bonding between the polymeric components, yielding insoluble species, which are termed polymer–polymer or interpolymer complexes. The characteristics of the complexes, including composition, yield and glass transition, are listed in Table 2.

The complexes yields are in the range of 52–96% and 13–89% for SMA50/PVP and SMA28/PVP, respectively. One should note that the yields are lower for SMA28/PVP than the SMA50/PVP complexes. It is clear that the copolymer SMA which contains more acid groups will develop more specific interactions with the PVP and then the complex formation will be promoted.

Additionally, the composition of the SMA28/PVP complexes depends on the feed composition of the solution from which it is formed. At the opposite the yields of the SMA50/PVP complexes, reached the maximum at the (3/7) weight ratio composition which stays constant till (8/2) one.

There are several methods to determine the complex stoichiometry. In our systems, the elemental analysis is an appropriate tool because PVP has in its monomeric unit a nitrogen atom, which does not exist in SMA28 and SMA50. The obtained results show a close correlation to 2:1 and 1:1 stoichiometry for SMA28/PVP and SMA28/PVP complexes, respectively. Similar results were obtained by considering the maximum yield value for SMA28/PVP and SMA50/PVP complexes which were obtained for 0.7 and 0.5 molar fraction of acidic copolymer content, respectively.

3.2. Glass transition

The complexes formed by mixing the pre-existing polymers are characterized by a well-defined stoichiometry which is usually independent of the composition of the starting mixture, display thermal and mechanical properties that differ significantly from those of the individual polymeric components [25]. Furthermore, the glass transition temperatures of SAM28, SAM50 and PVP are 165, 214 and 167 °C, respectively. However, in spite of the close T_g’s value of SAM28 and PVP polymers, the study of the SAM28/PVP system was possible according to the very high values of the complexes’ T_g.

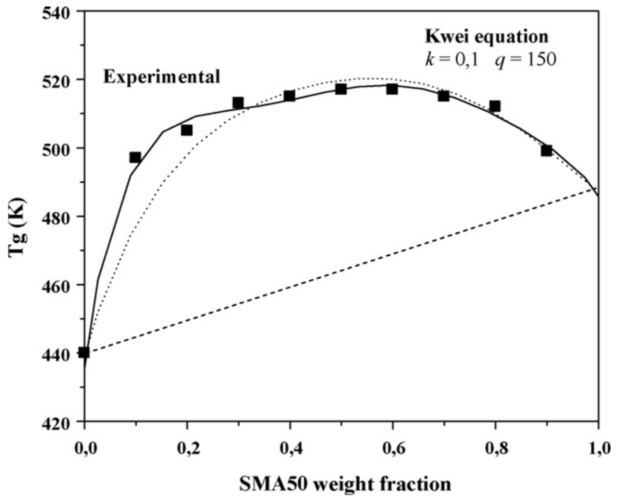


Fig. 1. Plot of the glass transition temperatures of SMA50/PVP complexes as a function of the feed compositions of SMA50 (■). Dashed curve is a prediction of Kwei equation with $k = 0.1$ and $q = 150$.

All prepared complexes in this work display two different T_gs’. The first one belongs to PVP phase whereas the second refers to the complexed PVP phase, which appears at a higher temperature than that of pure PVP. Nevertheless, the uncontrolled process of complex formation, during the mixing of relatively concentrated solutions can lead to its high heterogeneity. Some parts of macro-chains are inaccessible to the other polymer because of high sample gelation and trapping of functional groups in network [26].

The T_g’ s values of SMA/PVP complexes are also re-plotted with respect to the SMA composition. Figs. 1–4 reveal the T_g–composition relationship for SMA28/PVP and SMA50/PVP complexes, respectively.

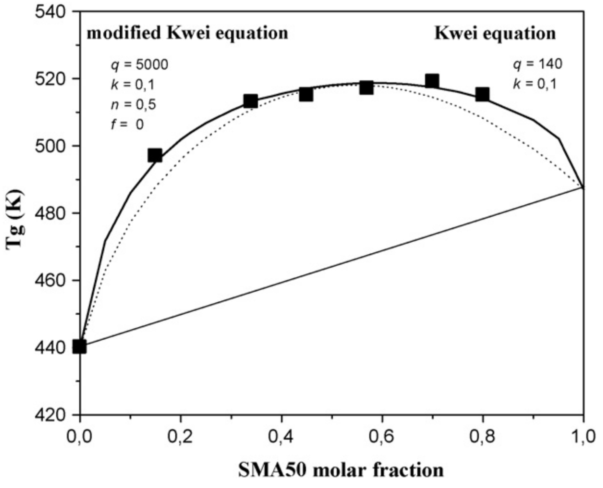


Fig. 2. Plot of the glass transition temperatures of SMA50/PVP complexes as a function of the bulk compositions of SMA50 (■). Dashed curve is a prediction of Kwei equation with $k = 0.1$ and $q = 140$. Solid line corresponds to theoretical T_g calculated by modified Kwei equation.

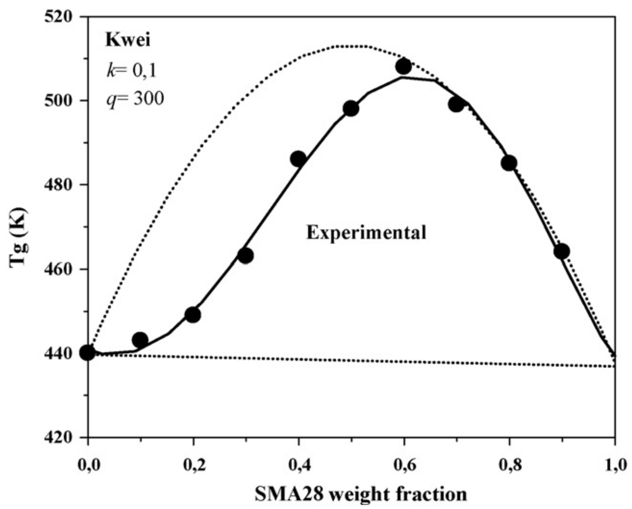


Fig. 3. Plot of the glass transition temperatures of SMA28/PVP complexes as a function of the feed compositions of SMA28 (●). Dashed curve is a prediction of Kwei equation with $k = 0.1$ and $q = 300$.

For both investigated systems, the T_gs of the complexes are higher than those predicted by the linear additivity rule. It is clear that positive deviation from the linearity suggests strong hydrogen-bonding interactions between SMA and PVP, restricting chain motion and thereby raising the T_g. Furthermore, additional evidence and discussion of hydrogen-bonding in SMA/PVP complexes will be shown later in FTIR section.

The glass transition of the miscible blends and its changes with the blend composition can be described by several empirical equations, such as those proposed by Gordon–Taylor [27], Braun and Kovacs [28], Fox [29], Couchman [30] and by Kwei [31]. The most employed is the Kwei equation,

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

where T_g is the blend glass transition, T_{g1} and T_{g2} are those of the pure components and w_i the weight fraction of component i, which is particularly suited to systems with specific interactions. The adjustable quantity q could be assigned as a measure of the strength of the specific interactions in polymer blends. This parameter is positive when the interactions between chains of different polymers are stronger than those between chains of the same polymer, otherwise $q < 0$. In this study, q obtained in these systems is always positive, which suggests that the intermolecular hydrogen-bonding interactions between pyrrolidyl and carboxylic acid are stronger than the dimeric self-associated acid ones. Since the parameter k is a fitting constant.

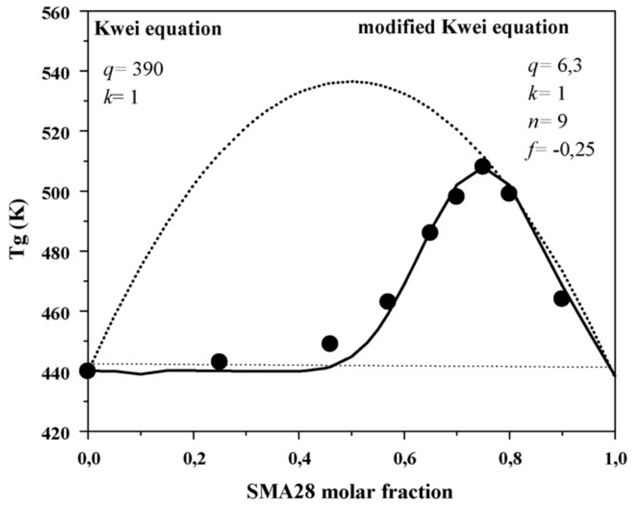


Fig. 4. Plot of the glass transition temperatures of SMA28/PVP complexes as a function of the bulk compositions of SMA28 (●). Dashed curve is a prediction of Kwei equation with $k = 1$ and $q = 390$. Solid line corresponds to theoretical T_g calculated by modified Kwei equation.

The maximum T_gs' values in SMA28/PVP and SMA50/PVP systems are obtained for 75 and 50 mol% of acid copolymer content, respectively. This result confirms that the ideal complexes' ratios are 2:1 and 1:1, respectively, and supports the suggestion that the number of connections between the interacting copolymers is maximised at a given polymer–polymer ratio.

However, when the feeds approximate this ratio, the complex yield should be at its highest value that should give a tightly bound and thus leading to a high complex's T_g. Moreover, the composition of the resultant complex HSMA28/PVP appears to strive towards an ideal level which is somewhat different than 1:1 molar ratio of polymers in the complex. Consequently, it appears as a narrowing of the plot of T_g against molar complex composition and the interpolymer complexes form the S-shaped behaviour with the presence of an inflection in the curve (see Figs. 2 and 4).

Additionally, the HSMA28/PVP complexes do not fall within the scope of any of the usual models proposed for polymer blends. Since it is not possible for any system described by these models to show a maximum, minimum or inflexion, this is why a new model which fits the data more closely is required (see Figs. 1–4).

The Kwei Eq. (1), contains almost all necessary elements to effectively model a system where the polymer chains interact to some extent and could form the basis of any extended model. The experimental data for polymer complexes show the curve resulting, when T_g is plotted against composition to be asymmetric, requiring the value of k to be maintained. These same curves also have an exaggerated form of the S-shape which the Kwei model describes so well, meaning that the value of q is also valid. However, since the number of interactions occurring in the formation of a polymer complex is different, and have higher, order than those occurring during the formation of polymer blend, it should be logical to state that the elements of the model equation are at a different order. This is why the parameter n was needed.

One more fact needs to be accounted, the maxima of the T_g–composition curve does not fall within the stoichiometric polymers ratio in all cases. Then the most effective method is to include a shifting factor f which allows the deviation of the peak maximum of 1:1 molar complex ratio and the modified Kwei equation may be taken as an expansion of the original one.

Hence, for the systems that present very strong interpolymers interactions, Harding and Cowie [24] have proposed a slightly modified version of Kwei Eq. (1) by including two additional empirical parameters:

$$T_g = \frac{(w_1 + f)T_{g1} + k(w_2 - f)T_{g2}}{(w_1 + f) + k(w_2 - f)} + (q(w_1 + f)(w_2 - f))^n \qquad (2)$$

a shift factor f which describes a deviation of the T_g–composition curve of the one to one polymer–polymer composition and a parameter n which indicates the degree of affinity of the polymers for each other. The values of n and f are truly empirical values but still provide a method for the comparison of the relative strengths of polymer–polymer bonds in a pre-formed complex. This model fits the experimental data most closely, where there is a high degree of interaction between the two polymers.

This new model was designed to explain the simplest mathematical relation for a physical property between a pair of polymers producing a small and regular deviation across the entire composition range of the complex [23,24].

The best fitting of (k, q, n, f) parameters given by the modified Kwei Eq. (2) for SMA28/PVP and SMA50/PVP systems are ($k = 1.0$; $q = 6.3$; $n = 9$; $f = -0.25$) and ($k = 0.1$; $q = 5000$; $n = 0.5$; $f = 0$), respectively. According to these results, the value $f = 0$ obtained for SMA50/PVP system, means that the polymers ratio is 1:1. This is why the modified Kwei equation fitting is close to the initial Kwei equation, as it can be seen in Figs. 1 and 2. On the other hand, the value of $n = 0.5$ obtained by modified Kwei equation, could mean that only one of the two acidic group of the maleic acid is concerned with the interaction since the second one becomes free.

At the same time, the value $f = -0.25$ obtained for the system SMA28/PVP is an indication that the complex composition is not 1:1. Thus the value of n which is higher in SMA28/PVP complexes indicates that there are more backbone linkages in this system than in the SMA50/PVP one.

Another fact has to be highlighted; by means of the Kwei equation the parameter q is considered as the measure of the strength of the interpolymer interactions but in the modified Kwei equation the meaning of the parameter q should not be the same. In that case it becomes a fitting parameter and the parameter n which was stated by Cowie et al. [24] as a degree of linkage between the complementary polymers will be considered as the new measure of the interpolymer strength.

Thus we can conclude that the value of the parameter n which is higher in SMA28/PVP ($n = 9$) system than the SMA50/PVP ($n = 0.5$), confirms the presence of stronger interpolymer interactions in the former system.

3.3. FTIR characterization of the complexes

The FTIR spectroscopy is one of the powerful tools used to investigate the specific intermolecular interactions [32,33]. The nature of the interpolymer interactions between SMA28 and SMA50 with PVP was examined by FTIR. According to the chemical structure of the polymers implicated in the interpolymer complexation process Scheme 1 and to the earlier discussion on the thermal analysis results, there should be specific interactions leading to the noted positive deviation of the linear T_g–composition relationship for SMA/PVP complexes. The FTIR spectra of different ratios of SMA28/PVP complexes are presented in the carbonyl stretching region in Fig. 5(a). Previous FTIR studies [34] showed that dry PVP copolymer presented a band at 1680 cm^{-1} called amide-I which is a combined mode of the C=O and C–N stretch. Furthermore, Mi et al. [35] stated that absorption of moisture by PVP which presents highly hydrophilic proprieties displaced this band to the lower frequencies. In this study we will refer the band at 1660 cm^{-1} to the carbonyl stretch of PVP. Furthermore the spectra of the SMA copolymer presented in Fig. 5(a), shows that the two bands situated at 1885 and 1785 cm^{-1} corresponding to maleic anhydride groups have almost disappeared and a broad band that extends over the 1740–1696 cm^{-1} range with a maximum at about 1729 cm^{-1} that corresponds to an overlapping of the free and the hydrogen bonded carbonyl groups [36]. The peak frequency of this broad band decreases with the increasing of PVP content in the complexes. We can then conclude that the addition of PVP in

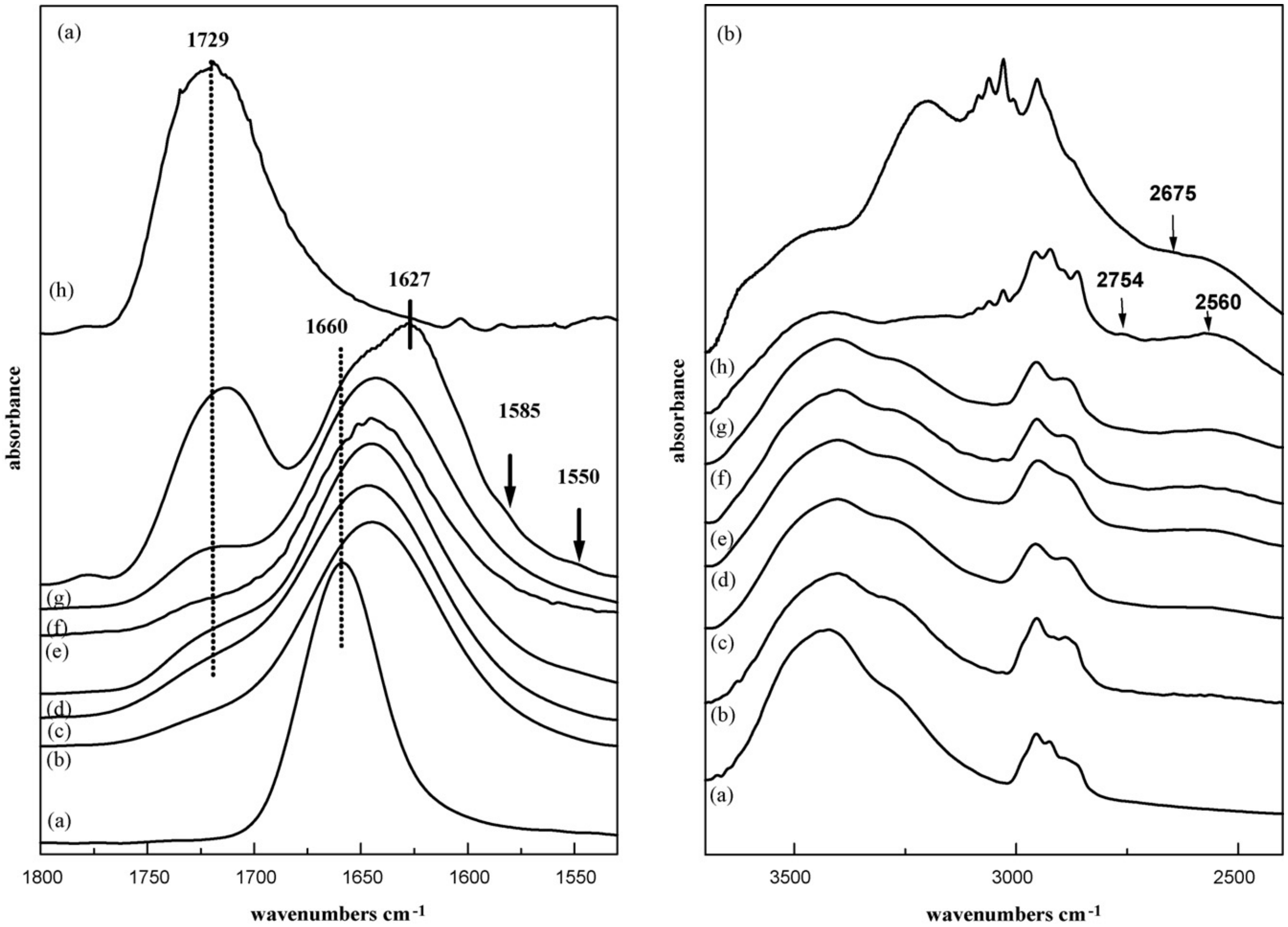


Fig. 5. Infrared spectra of SMA28/PVP complexes at room temperature: (a) in the carbonyl stretching region and (b) in the hydroxyl-stretching region. (a)0, (b)10, (c)20, (d) 30, (e) 50, (f) 60, (g) 80 and (h) 100 wt% of SMA28.

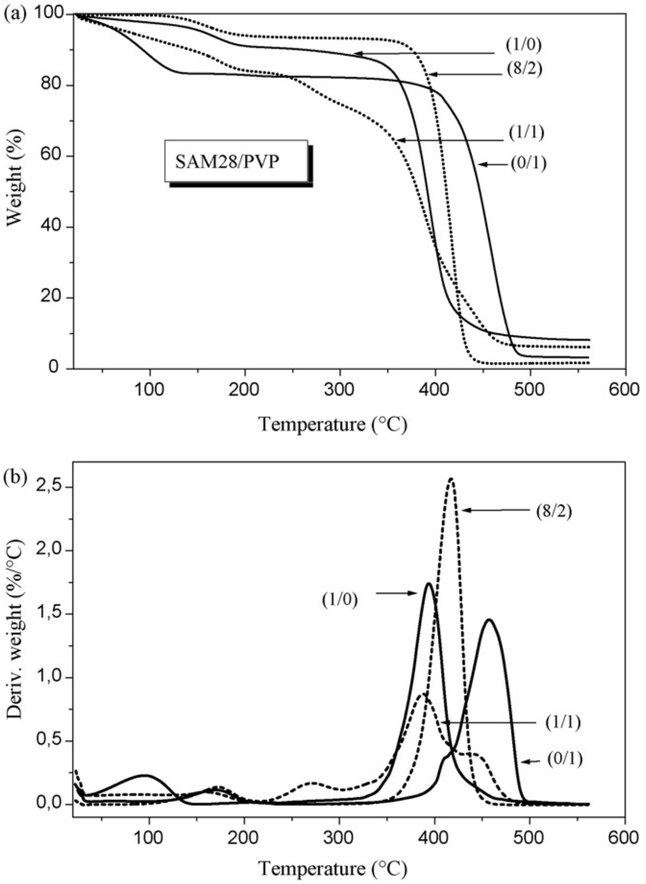


Fig. 6. Thermogravimetric curves of SMA28/PVP complexes in 1/0, 8/2, 1/1 and 0/1 weight ratio: (a) weight loss percent and (b) derivative curves.

the complexes lead to the destruction of a part of self-associated acidic groups and a redistribution of them to the hetero associated ones.

In all cases, FTIR spectrum of the complexes is not a simple superposition of the spectra of the pure components. The shape of C═O absorption bands for SMA/PVP system depends on the sample composition and the carbonyl bands in the complexes are broader than that in pure SMA and PVP. This is an evidence of a large distribution of interacting components that leads to strong interactions. Furthermore, in samples with dominant amount of one component, the carbonyl band is composed of the band of complexed and the band of the non-complexed polymer in excess.

In the same time the intensity of the carbonyl band centred at 1729 $\mathrm{cm^{-1}}$, corresponds to the SMA28 carboxylic acid, that shifts to the lower wavenumbers and decreases with the increasing of PVP content in the complexes. This is probably due to the destruction of dimeric acid–acid interactions in SMA28 copolymer and the appearance of acid–base interactions between the hydroxyl group of carboxylic acid in SMA28 and the PVP carbonyl group.

When the PVP carbonyl group is hydrogen bonded to the SMA28 hydroxyl, the PVP carbonyl absorption band centred at 1660 $\mathrm{cm^{-1}}$ also shifts to the lower wavenumbers at around 1643 $\mathrm{cm^{-1}}$, as can be seen in all complexes spectra. The intensity of this band increases upon increasing SMA content in the complexes and it leads to 1627 $\mathrm{cm^{-1}}$ for the (80/20) weight ratio of SMA28/PVP complex, see Fig. 5(a) curve (g), suggesting the presence of ionic interactions. This result is confirmed by the appearance of asymmetric vibration signals of carboxylate anions situated at 1550 and 1585 $\mathrm{cm^{-1}}$ which are assigned to the protons transfer from the carboxylic groups of SMA to the nitrogen atoms of PVP.

Moreover, the chemical displacement between the free and associated carbonyl groups was taken as the average strength of hydrogen-bonding interactions in the blends [37] corresponding to $\Delta\upsilon = 33\ \mathrm{cm^{-1}}$ and $\Delta\upsilon = 19\ \mathrm{cm^{-1}}$ for SAM28/PVP and SAM50/PVP systems, respectively in the PVP carbonyl region. This indicates that the hydrogen-bonding is rather stronger in the former complexes, as predicted before by the modified Kwei equation which gives higher value of the parameter n for SAM28/PVP ($n = 9$) system than SMA50/PVP ($n = 0.5$).

The range of hydroxyl stretching vibration 4000–3000 $\mathrm{cm^{-1}}$ is not considered because of the difficulty of removing the water residue completely. Therefore the long drying in the vacuum at an elevated temperature is dangerous for the polyacid structure because cyclic anhydride can be formed. Fig. 5(b) shows FTIR spectrum of pure SMA28, PVP and SMA28/PVP complexes in the range 3000–2400 $\mathrm{cm^{-1}}$ of hydroxyl region. The satellite band, enhanced by Fermi resonance attributed to the self-associated hydrogen bond of dimeric acid groups appears in the pure SMA28 spectra at about 2675 $\mathrm{cm^{-1}}$ and displaces slightly to the low frequency in the SMA28/PVP complexes. We may therefore assign this shift to the pyrrolidone–acid interaction between the hydroxyl groups of SMA28 and the nitrogen atoms of the PVP copolymer. Thus, a new peak at 2754 $\mathrm{cm^{-1}}$ corresponding to the protonated tertiary amine groups, is observed in Fig. 5(b) curve (g), showing that some of PVP nitrogen atoms have been protonated in the complex SMA28/PVP of the (80/20) weight ratio.

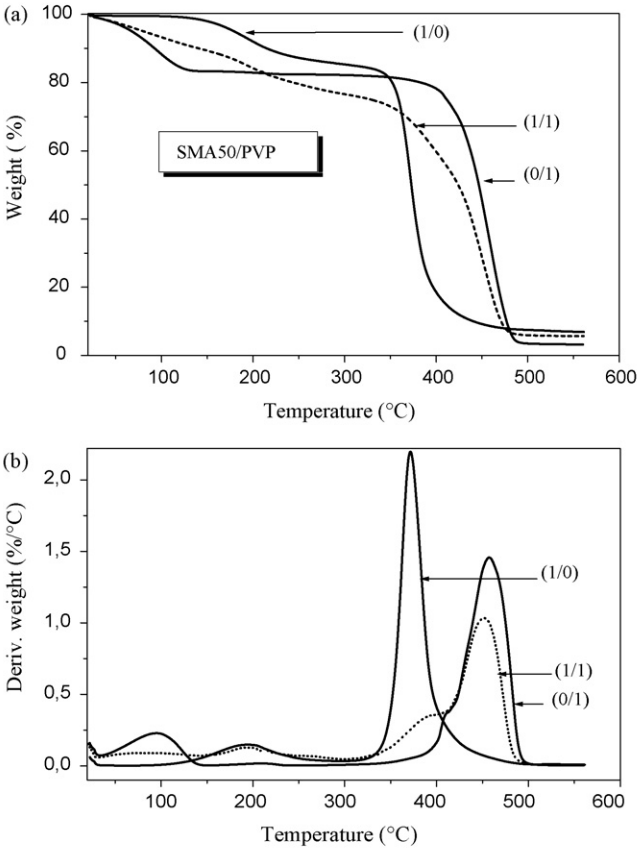


Fig. 7. Thermogravimetric curves of SMA50/PVP complexes in 1/0, 1/1 and 0/1 weight ratio: (a) weight loss percent and (b) derivative curves.

Table 3
Thermogravimetric parameters of SMA28, SMA50, PVP and their complexes at different ratios

Feed ratio	Stage 1		Stage 2		Last stage	
	T_{max} (°C)[a]	ΔW (wt%)[b]	T_{max} (°C)[a]	ΔW (wt%)[b]	T_{max} (°C)[a]	Residual weight (%)
SMA28/PVP						
0/1: 2 stages	99	16.68	–	–	457	3.22
1/9: 3 stages	79	14.60	244	19.01	450	5.25
3/7: 5 stages	81	10.67	178	14.95	443	7.82
1/1: 3 stages	172	16.29	273	23.07	390	6.20
6/4: 3 stages	176	15.60	284	22.56	398	5.13
7/3: 3 stages	178	15.34	276	24.43	400	6.83
9/1: 2 stages	162	06.27	–	–	418	1.67
1/0: 2 stages	169	9.33	–	–	394	9.46
SMA50/PVP						
2/8: 3 stages	94	12.78	245	19.93	451	4.58
3/7: 3 stages	78	12.67	249	18.30	448	3.70
4/6: 3 stages	132	14.12	221	22.35	452	5.10
1/1: 3 stages	193	23.10	391	43.84	452	6.15
6/4: 3 stages	182	22.60	395	43.02	441	6.43
7/3: 3 stages	100	15.49	235	21.54	452	6.15
1/0: 2 stages	193	14.30	–	–	372	7.53

[a] Maximum temperature values for each step.
[b] Total weight loss percentage at the end of the step.

3.4. Thermogravimetric measurements

The thermogravimetric curves of the pure polymers are shown in Figs. 6 and 7. The degradation of PVP occurs in two steps. The first step, less than 100 °C corresponds to the loss of water by dehydration. This step is consistent with the high hydrophilic character of the homopolymer since the presence of a high amount of moisture in PVP was also evidenced by FTIR study. In the second step from 320 to 500 °C there are two peaks, the first is connected probably with the loss of ammonia by imidization and last corresponds to decarboxylation and carbonisation processes accompanying the main chain scission.

The thermogravimetric scans of pure SMA28 and SMA50 show two degradation steps. The first step from the temperature range 100–210 °C and 100–270 °C for SMA28 and SMA50, respectively. This step is assigned to the elimination of water adsorbed to the hydrophilic copolymers and to the anhydride ring formation in the main chain. The second step concerns the spectrum from 300 to 500 °C for both copolymers, assigned to the main chain scission.

The thermogravimetric behaviour of the SMA28/PVP and SMA50/PVP complexes is displayed in Figs. 6 and 7. The reported data suggest that the thermal degradation behaviour is mainly controlled by the hydrogen-bonding in the system and as a result their degradation can be considered as a multistage process.

After the breakage of most hydrogen bonds, the degradation of complex components starts. The first stage, less than 250 °C, corresponds to anhydride formation. The second which proceeds from 250 to 340 °C is attributed to the loss of ammonia by imidization. Whereas, the main chain scission process occurs in the third stage from 340 to 450 °C, while above 450 °C carbonisation prevails. The thermogravimetric parameters of the complexes are summarized in Table 3.

On the other hand, the degradative behaviour of SMA28/PVP (80/20) complex deserves a special comment since it was the only system which has the first onset temperature higher than those of the pure acidic copolymer. Then we related that to a large number of hydroxyl groups of SMA28 strongly hydrogen bonded to PVP and the ionic interactions which also occurred in this system, decreasing the distance between the interacting components on the main chain and enhancing the regularity of the macromolecular structure. When the extension of hydrogen-bonding is more important in a particular sample, its break becomes more difficult and requires higher temperatures. Consequently the ionic interaction increase the thermal stability of the complexes.

4. Conclusions

It was found that SMA50/PVP (1:1) and SMA28/PVP (2:1) complexes exhibit different behaviours. The T_g–composition curve does not conform to the usual accepted models proposed for polymer blends. A new model proposed by Hardling and Cowie based on the modified Kwei equation was used to fit the data more closely. It accounts for the fact that in tightly complexes' bounds the ideal molar ratio may not be 1:1 in all cases and a new model is needed to quantify very strong specific interactions in the interpolymer complexes. The fundamental difference between these two materials must be in the way that the specific interactions are distributed.

According to the values of n and q obtained, it seems reasonable to conclude that the inter-associated hydrogen bonds dominate and occupy a large scale in SMA28/PVP (2:1). This result is corroborated by FTIR study as evidenced by high displacement of specific bands. The thermal behaviour of these systems seems to be also controlled by the hydrogen-bonding and the presence of ionic interaction will improve their thermal stability.

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References

[1] E. Tsuchida, K. Abe, Adv. Polym. Sci. 45 (1982) 1.
[2] E. Bekturov, L. Bimendina, Adv. Polym. Sci. 41 (1981) 99.
[3] P. Dubin, J. Bock, R. Davis, D. Schulz, C. Thies, Macromolecular Complexes in Chemistry and Biology, Springer, Berlin, Heidelberg, New York, 1994.
[4] M. Hara, Polyelectrolytes: Science and Technology, Marcel Dekker, New York, 1993.
[5] G. Challa, in: P. Lemstra (Ed.), Integration of Fundamental Polymer Science and Technology, vol. 5, Elsevier Applied Sciences, London, 1990, p. 85.
[6] J. Rodriguez-Parada, V. Percec, Macromolecules 19 (1986) 55.
[7] H. Wang, W. Li, Y. Lu, Z. Wang, W. Zhong, J. Appl. Polym. Sci. 61 (1996) 221.

[8] J. Dai, S.H. Goh, S.Y. Lee, K.S. Siow, Polym. J. 26 (1994) 905.
[9] Y. Liu, S.H. Goh, S.Y. Lee, C.H.A. Huang, Macromolecules 32 (1999) 1967.
[10] Z. Zhong, Q. Guo, Polym. Int. 41 (1996) 315.
[11] L. Wang, E. Pearce, T.K. Kwei, J. Polym. Sci. B Polym. Phys. 29 (1991) 619.
[12] X. Luo, S. Goh, S. Lee, Macromolecules 30 (1997) 4934.
[13] E.A. Bekturov, L.A. Bimendina, Adv. Polym. Sci. 41 (1981) 99.
[14] Y. Osada, Adv. Polym. Sci. 82 (1987) 2.
[15] N. Bouslah, R. Hammachin, F. Amrani, Macromol. Chem. Phys. 200 (1999) 678.
[16] N. Bouslah, F. Amrani, Express Polym. Lett. 1 (2007) 44.
[17] N. Bouslah, R. Hammachin, N. Haddadine, F. Amrani, J. Appl. Polym. Sci. 108 (2008) 3256.
[18] S. Ourdani, F. Amrani, Macromol. Chem. Phys. 201 (2000) 2458.
[19] R. Bouyahia, F. Metref, S. Djadoun, Macromol. Symp. 263 (2008) 86.
[20] A. Habi, S. Djadoun, Thermochim. Acta 469 (2008) 1.
[21] A. Habi, S. Djadoun, Eur. Polym. J. 35 (1999) 483.
[22] N. Haddadine-Rahmoun, F. Amrani, V. Arrighi, J.M.G. Cowie, Eur. Polym. J. 44 (2008) 821.
[23] J.M.G. Cowie, M.T. Garay, D. Lath, I.J. McEween, Br. Polym. J. 21 (1989) 81.
[24] P.D. Harding, Ph.D. Thesis, A Study of the Relationship Between Water, Water Soluble Polymers and Their Inter-polymer Association Complexes, Heriot-Watt University, Edinburgh, 1997.
[25] L. Gargallo, N. Gatica, D. Radicǐ, Int. J. Polym. Mater. 27 (1994) 107.
[26] H. Kaczmarek, A. Szalla, A. Kaminska, Polymer 42 (2001) 6057.
[27] M. Gordon, J.S. Taylor, J. Appl. Chem. 2 (1952) 493.
[28] G. Braun, A.J. Kovacs, Variation in the glass transition temperature of binary systems of statistical distribution. In: J.A. Prins (Ed.), Physics of Non-crystalline Solids. Proceedings of the International Conference, 1965, pp. 303–318.
[29] T.G. Fox, Bull. Am. Phys. Soc. 1 (1956) 123.
[30] P.R. Couchman, Macromolecules 11 (1978) 1157.
[31] T.K. Kwei, J. Polym. Lett. Ed. 22 (1984) 307.
[32] M. Hara, J.L. Wu, A.H. Lee, Macromolecules 21 (1988) 2214.
[33] N. Bouslah, N. Haddadine, D. Bendiabdallah, F. Amrani, Polym. Bull. 42 (1999) 701.
[34] P. Molyneux, Water-soluble Synthetic Polymers, vol. 1, CRC Press, Boca Raton, 1983, p. 75 (Chapter 3).
[35] C. Lau, Y. Mi, Polymer 43 (2002) 823.
[36] M.M. Coleman, J.F. Graft, P.C. Painter, Specific interactions and the miscibility of polymer blends, Technomic Lancaster, PA, 1991.
[37] E.J. Moskala, D.F. Varnell, M.M. Coleman, Polymer 26 (1985) 228.