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Miscibility and thermal behaviour of poly(styrene-*co*-methacrylic acid)/poly(isobutyl methacrylate-*co*-4-vinylpyridine) mixtures

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Abstract

The miscibility and the thermal behaviour of binary mixtures of poly(styrene-*co*-methacrylic acid) containing 12 or 29 mol.% of methacrylic acid (SMA-12 or SMA-29) with poly(isobutyl methacrylate-*co*-4-vinylpyridine) containing 20 mol.% of 4-vinylpyridine (IBM4VP-20) as blends or interpolymer complexes were investigated by differential scanning calorimetry, thermogravimetry and FTIR spectroscopy. The results showed that, depending on the nature of the solvent used in the mixture and the density of the specific interacting species introduced within the polymer matrices, miscible polymer blends or interpolymer complexes were obtained.

The single T_g observed with all the studied blends or interpolymer complexes is an evidence of their miscibility. The positive deviation of the T_g of the blends and the complexes from the weight average of the constituents T_gs and the improved thermal stability of the SMA29/IBM4VP-20 complexes as compared to their corresponding blends is mainly due to the presence of stronger specific interactions of hydrogen bonding type that occurred between the carboxylic groups of the SMA-29 and the 4-vinylpyridine of the IBM4VP-20 and to the way these specific interactions are distributed. A quantitative analysis of these interactions was carried by FTIR above the glass transition temperature of the constituents of the (85/15) SMA-29/IBM4VP-20 blend in the 1850–1570 cm^{-1} region.
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Keywords: Miscibility; Blends; Thermal degradation; Poly(styrene-*co*-methacrylic acid); Poly(isobutyl methacrylate-*co*-4-vinylpyridine); FTIR spectroscopy; DSC

1. Introduction

It is known and reported in the literature that poly(isobutyl methacrylate) (PIBMA) of a glass transition temperature T_g at about 60 °C, noted for its relatively low thermal stability as most polyalkylmethacrylates, is immiscible with polystyrene (PS). An attempt to improve some of its properties among others its T_g through an enhancement of its miscibility with PS that possesses a better thermal stability and much lower water absorption, was to introduce specific groups such as acrylic acid or methacrylic acid within the polystyrene matrix by copolymerization [1–4] so that interpolymer interactions would occur between the ester groups of PIBMA and the carboxyl groups introduced within these copolymers. Unfortunately, due to the

presence of bulky groups within the PIBMA, the attractive interactions between the two components of the blend and the repulsive styrene-methacrylic acid or styrene-acrylic acid interactions were not sufficient to induce the miscibility of this pair of polymers though small amount only of carboxylic groups introduced within the polystyrene matrix led to miscible blends of these latter with poly(ethyl methacrylate) [5].

The poly(alkyl methacrylates) are known to degrade differently, depending on the alkyl side chain of the ester. Some of them degrade through a single step with formation of monomer while a more complex mechanism of decomposition is reported with others.

We have previously showed that the incorporation of only 12 mol.% of methacrylic acid and 10 mol.% of 4-vinylpyridine within polystyrene and poly(isobutyl methacrylate), respectively, led to miscible SMA-12/IBM4VP-10 blends [4]. Since increasing the amount of interacting species within the polymer chains would usually form interpolymer complexes [6],

Table 1
Characteristics of the different random copolymers

Copolymer	Composition (mol%)				T_g (°C)	$[\eta]$ (dl/g)
	IBM	4VP	S	AM		
IBM4VP-10	90	10	–	–	76	1.38
IBM4VP-20	80	20	–	–	86	1.20
SMA-12	–	–	88	12	125	0.88
SMA-29	–	–	71	29	156	0.97

we have in the present contribution introduced by free radical copolymerization 20 mol.% of 4-vinylpyridine within the poly(isobutyl methacrylate) and then, respectively, investigated by differential scanning calorimetry and thermogravimetry the miscibility and the thermal behaviour of binary mixtures of SMA-12/IBM4VP-20 and SMA-29/IBM4VP-20 as blends or interpolymer complexes. The thermal behaviour of the (85/15) SMA-29/IBM4VP-20 blend was also carried by FTIR in the 50–220 °C temperature range from a quantitative analysis of the hydrogen bonding interactions that occurred between the two copolymers within this blend in the 1650–1570 cm^{-1} region and the identification of the anhydrides that are formed in the carbonyl region.

2. Experimental

2.1. Materials

Random copolymers of poly(isobutyl methacrylate-*co*-4-vinylpyridine) containing 10 or 20 mol.% of 4-vinylpyridine (IBM4VP-10 or IBM4VP-20) and poly(styrene-*co*-methacrylic acid) containing 12 or 29 mol.% of methacrylic acid) (SMA-12 or SMA-29) were prepared by solution free radical polymerization at 60 °C using azobis-isobutyronitrile (AIBN) as the initiator, keeping the conversion low. The copolymers were purified by two dissolution/reprecipitation cycles and dried under vacuum for several days.

2.2. Characterizations

The styrene (S) and 4-vinylpyridine (4VP) contents in the SMA and IBM4VP copolymers were determined by UV spectroscopy. Intrinsic viscosities of these copolymers were determined at 25 °C in THF using an Ubbelohde viscometer. The results of these characterizations and the glass transition temperature of these copolymers obtained by DSC traces are summarized in Table 1.

2.3. Preparations of blends and interpolymer complexes

Blends of different ratios of IBM4VP-10/SMA-12, IBM4VP-20/SMA-12 and IBM4VP-20/SMA-29 were prepared by coprecipitation in heptane. These blends, dried to constant weight in a vacuum oven at 50 °C during several days to remove traces of solvent, were used in the DSC and TGA analysis.

SMA-12, SMA-29, IBM4VP-10 and IBM4VP-20 were separately dissolved in THF or Butan-2-one to form dilute solutions.

Appropriate amounts of acidic (SMA-12 or SMA-29) and basic (IBM4VP-10 or IBM4VP-20) solutions were mixed together by drop wise addition of SMA solution to IBM4VP-10 or IBM4VP-20 solutions. Depending on the nature of the solvent and the densities of the interacting species introduced within the polymer chains, a homogeneous phase or interpolymer complexes in the form of precipitates were observed with these mixtures.

2.4. DSC measurements

The glass transition temperatures T_g of these copolymers and of their blends or complexes were measured using a PerkinElmer DSC-7 at a heating rate of 20 °C/min under a nitrogen atmosphere. 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.

2.5. Thermal degradation studies

Thermogravimetric measurements were performed on a TGA Q50 from TA instruments using nitrogen as a purge gas at a heating rate of 10 °C/min from room temperature to 500 °C. The amount of polymers or their mixtures as blends or precipitates used in these experiments was less than 15 mg.

2.6. FTIR measurements

Infrared spectra of SMA-12/IBM4VP-20 blends obtained as precipitates from heptane were determined at room temperature with a vertex 70 FTIR/ATR spectrometer using 60 scans at a resolution of 2 cm^{-1}. Thin films of the SMA-29 and its (85/15) blend with IBM4VP-20 were prepared from dilute solution in THF by casting on KBr disks. The disks were kept in a vacuum oven for several days at 60 °C until the solvent was removed. The FTIR spectra of the SMA-29 and SMA-29/IBM4V-P20 (85/15) blend were then recorded at a 2 cm^{-1} resolution and 60 scans, on heating from room temperature to 220 °C and then on cooling to 50 °C using a Nicolet 560 FTIR spectrometer equipped with a microprocessor-temperature and a processor controller Omega CN3201.

3. Results and discussion

3.1. SMA-12/IBM4VP-20 blends

Qualitative tests showed that homogeneous phases were observed when SMA-12 is mixed in all proportions with IBM4VP-20 in THF or butan-2-one in agreement with our previous results for SMA-12/IBM4VP-10 blends [4]. This may be considered as a preliminary evidence of the miscibility of these blends. Though transparent films were obtained when these blends were cast from either of these two solvents, it is known that the casting method may affect the glass transition temperature [7,8]. To minimize this effect, the glass transition temperature of the pure components and their blends of different ratios were determined from samples as precipitates from heptane.
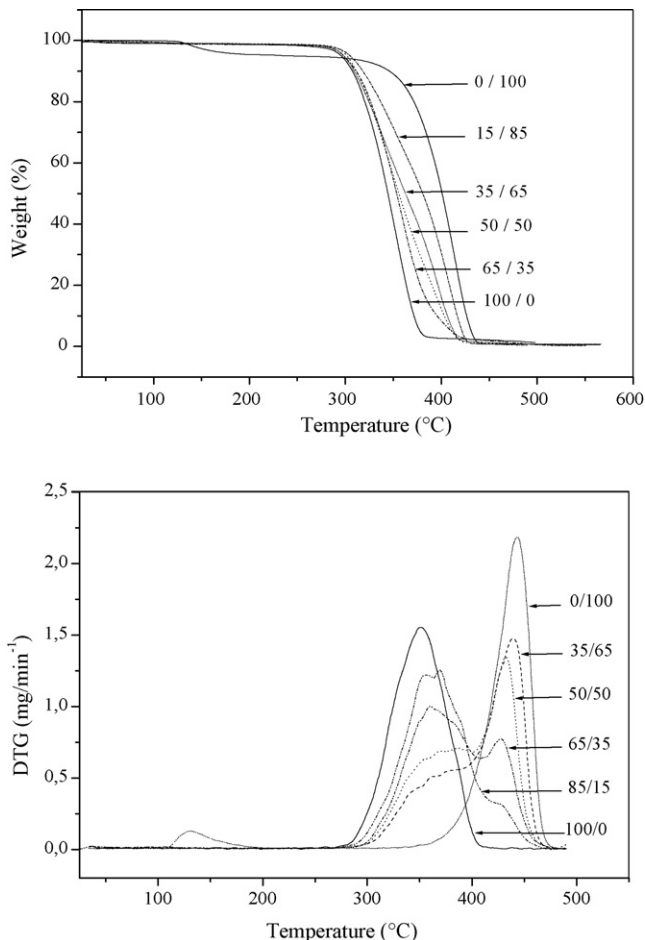
Fig. 1. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of SMA12 (0/100), IBM4VP-20 (100/0) and their blends of different ratios.

Prior to the DSC measurements, a thermogravimetric analysis was carried out for the SMA-12, IBM4VP-20 copolymers and their blends as precipitates. Fig. 1 shows the thermogravimetric (TGA) and derivative thermogravimetric (DTGA) curves of these copolymers and their blends containing 15, 35, 50 and 65% of SMA-12. IBM4VP-20 shows a single degradation step at $T_{max} = 352\,°C$ while two stages of degradation are displayed with the acidic SMA-12 copolymer. The first step of degradation, of very small weight loss amount, in the 100–150 °C temperature range, is assigned to loss of adsorbed water from the hydrophilic groups of the SMA-12. A higher initial degradation temperature is reported in the literature for pure polystyrene [9,10]. Any traces of anhydrides that might have been formed would appear at higher temperature. The introduction of 12 mol.% of methacrylic acid, diluted within the polystyrene matrix, did not affect considerably the main stage of degradation that occurs between 360 and 458 °C with a T_{max} at 443.5 °C. Zeliazkow [11,12] showed that the thermal degradation of copolymers of styrene with dicarboxylic acids depends on the stereoregularity of the carboxylic groups and that these copolymers degrade in two main stages.

Mixing SMA-12, a copolymer of higher temperature of maximum degradation rate with IBM4VP-20 is expected to improve

Table 2
Degradation temperatures of IBM4VP-20 (100/0), SMA-12 (0/100) and their blends of different ratios

Composition (%)	T_{onset} (°C)	T_{max} (°C)
00/100	406	444
35/65	329	440
50/50	327	432
65/35	329	428
85/15	327	369
100/00	314	352

the thermal stability of this latter within the resulting miscible blend due to the hydrogen bonding interactions that may occur between these two copolymers and act as physical cross-links. Table 2 summarizes the thermogravimetric parameters of the pure components and their blends. The blends of different ratios showed thermogravimetric and derivative thermogravimetric curves and degradation processes different from those corresponding to the pure components. As it can be seen, the degradation step in the 100–150 °C temperature range is not observed with the blends. The hydrophilic groups of the SMA-12 copolymer prefer to hydrogen bond to IBM4VP-20. The first stage showed from the DTGA curves three shoulders characteristic of an overlap of different degradative processes As the SMA-12 is progressively added to the IBM4VP-20, the onset temperature and the T_{max} of the first degradation stage, observed with all these blends, shifted toward higher temperature as compared to the one of IBM4VP-20. The T_{max} of the second stage of degradation of the blends is observed before that of the SMA-12 and increased as its proportion increases in the blend. This suggests an improved thermal stability of these blends. Based on the thermal degradation results, a DSC analysis was performed to study the miscibility of these blends. It is admitted that a single compositionally dependent glass transition temperature is an indication of miscibility. The single T_g observed with all the studied blends (SMA-12/IBM4VP-10 and SMA-12/IBM4VP-20) is an evidence of their miscibility. As shown in Fig. 2, the T_g of these blends deviate positively from the weight average
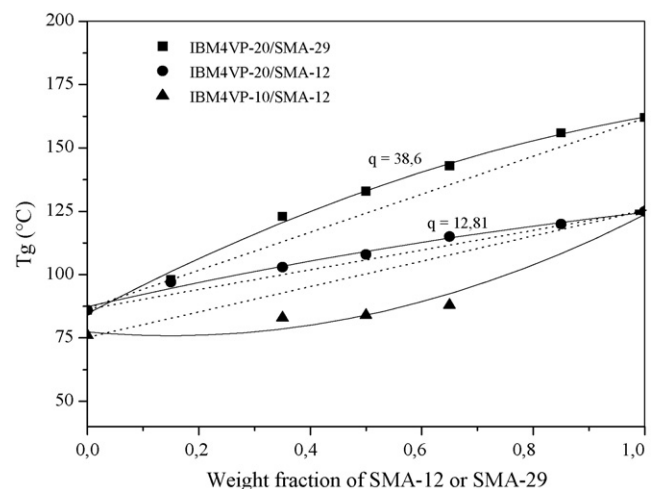

Fig. 2. T_g-composition of IBM4VP-10/SMA-12, IBM4VP-20/SMA-12 and IBM4VP-20/SMA-29 blends.

of the constituents T_gs. This is due to the presence of specific interactions that occurred between the carboxylic groups of the SMA-12 and the 4-vinylpyridine and eventual ester groups of the IBM4VP-20. Since SMA-12 is immiscible with poly(isobutyl methacrylate) [3], the ester-carboxylic groups are weak and the miscibility of SMA12/IBM4VP20 blends is mainly due to pyridine–carboxylic group interactions. The intensity of these interactions is estimated from the Kwei constant q obtained from the equation below [13]:

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

where w_1, w_2, T_{g1} and T_{g2} are the weight fractions and glass transition temperatures of the constituents, respectively.

The obtained q value of 12.81 indicates that stronger interactions occurred between these two constituents of the blend as compared to those within SMA-12/IBM4VP-10 blends. The negative deviation observed with these latter blends is not due to the presence of any THF traces since all the T_g were obtained from the second scan but to weak and small number of specific interactions that occurred between the two copolymers which depends on the amount of carboxylic groups introduced within the SMA12. Such interactions of hydrogen bonding type that occurred between the carboxylic groups of the SMA-12 and the pyridine nitrogen atoms of the IBM4VP-20 are qualitatively evidenced at room temperature by FTIR by the appearance of a band at 1607 cm^{-1} characteristic of pyridine associated to carboxyl groups as shown in Fig. 3.

3.2. SMA-29/IBM4VP-20 mixtures

When IBM4VP-20 is mixed together with an acidic copolymer of higher content of methacrylic acid as with SMA-29 in
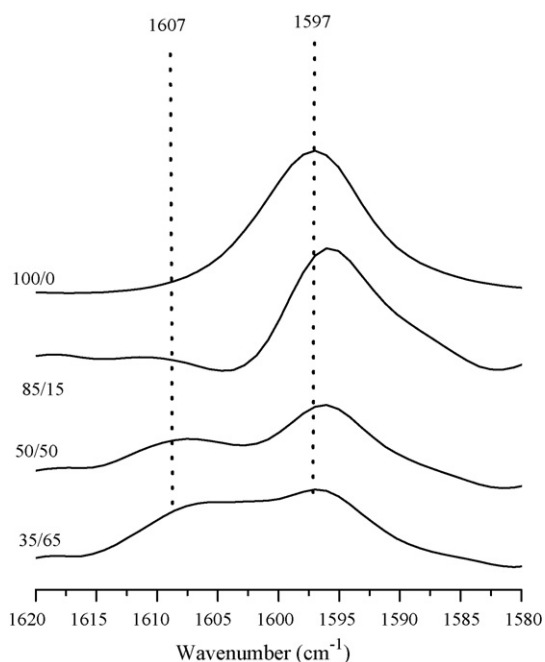

Fig. 3. FTIR spectra of IBM4VP-20 (100/0) and FTIR difference spectra (subtraction of PS) of IBM4VP-20/SMA-12 blends of different ratios in the range 1620–1580 cm^{-1}.
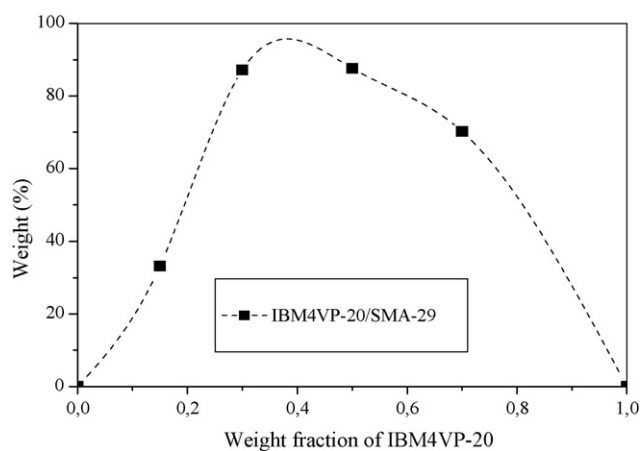

Fig. 4. Yield for IBM4VP-20/SMA-29 (■) complexes.

THF, homogeneous phases are observed from dilute to relatively concentrated solutions. As stated above, this could be considered as a qualitative indication of the miscibility of these blends. These copolymers behaved however differently when mixed in butan-2-one. Two phases are observed: a precipitate in equilibrium with a dilute phase containing mainly the solvent. This phenomenon that led to the formation of interpolymer complexes is due to a higher number of specific interactions that occurred between the two copolymers in butan-2-one than between copolymer-butan-2-one pairs. It is reported in the literature that the polymers of different nature are randomly mixed in a miscible blend but due to a higher number of interactions that occurred between them, they are paired in a complex [14]. Fig. 4 shows how the yield of these complexes varied with the initial feed composition.

The thermal behaviour of these two kinds of materials as blends or interpolymer complexes is investigated.

3.2.1. SMA-29/IBM4VP-20 blends

The TGA and DTGA curves of the SMA-29/IBM4VP-20 blends cast from THF are illustrated in Fig. 5. As it is seen, the blend composition affects the degradation process. The T_{max} of the second step is slightly shifted to lower temperature (401 °C). The DTGA curves revealed three or four degradation steps as the IBM4VP-20 composition increased in the blend. Two peaks are detected in the first temperature degradation region between 100 and 260 °C. The first peak with a maximum around 150 °C is attributed to the loss of adsorbed water which intensity progressively increases with the increase of IBM4VP-20. The second peak with a maximum around 210 °C corresponds to anhydride formation which is also evidenced by FTIR as shown in Fig. 6. The second degradation step (from 270 to 385 °C) with a T_{max} around 350 °C may be related to an overlap of decarboxylation and to the degradation of the main chain of IBM4VP-20. The last process that occurs at higher temperature which T_{max} (414 °C) shifts to lower temperature with an increase of IBM4VP-20 is attributed to the main degradation step of SMA-29. These results show that the thermal stability of the IBM4VP-20/SMA-29 blends cast from THF decreases with an increase of the IBM4VP-20. Katime and co-workers
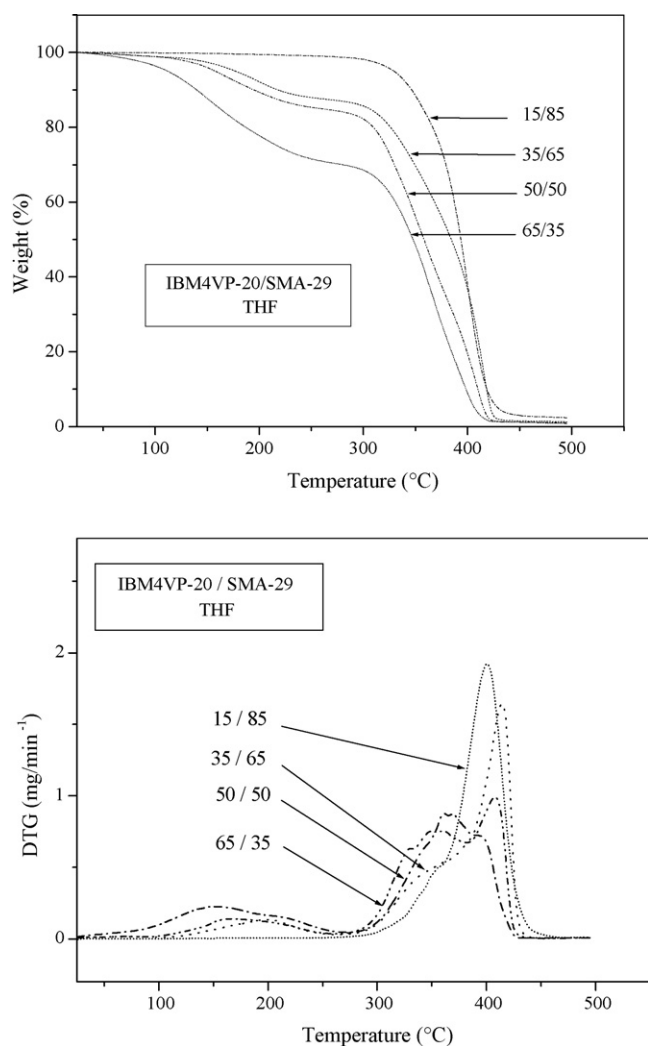
Fig. 5. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of IBM4VP-20/SMA-29 blends of different ratios cast from THF.

[15] reported similar observations for blends of poly(monoethyl itaconate) with poly(vinylpyridine)s.

We have in this study recorded FTIR spectra for the SMA-29 and its relatively stable (15/85) as cast blend containing the lowest IBM4VP-20 proportion on heating from room temperature to 220 °C and then on cooling to room temperature for this blend. In agreement with the TGA results, no anhydride were formed with the SMA-29 up to this temperature. A small amount of anhydride formed with the blend above from 200 °C, is confirmed as shown in Fig. 6 by the appearance of two new peaks at 1759 and 1801 cm^{-1}. It is worth noting the presence in this temperature range of the bands at 1742 and 1700 cm^{-1} characteristic of free and cyclic dimer carboxylic groups, respectively. This is an evidence of an incomplete dehydration.

A quantitative analysis of the hydrogen bonding interactions that occurred between the carboxylic groups of SMA-29 and the pyridine groups of IBM4VP-20 within the 85/15 blend was carried out above the glass transition temperature of the two constituents in the 1650–1580 cm^{-1} region. The fractions of the relative areas related to the two bands at 1597 and 1607 cm^{-1} characteristic of free and associated pyridine groups were determined using a Lorentzian spectral curve fitting procedure.

The fraction of free pyridine groups was calculated from the following relation [16]:

$$F_F^N = \frac{A_{1597}}{A_{1597} + (a_{1597}/a_{1607})A_{1607}} \quad (2)$$

where A_{1597} and A_{1607} are the areas of the bands at 1597 and 1607 cm^{-1}, respectively, a_{1597} and a_{1607} are the absorptivities of the two bands, assuming an absorptivity ratio of unity.

Fig. 7 shows the evolution of the fraction of the associated pyridine groups in the SMA-29/IM4VP-20 (85/15) blend with temperature on heating and cooling.

A decrease of the band intensity at 1606 cm^{-1} corresponding to the hydrogen-bonded pyridine–carboxylic groups is observed as the temperature is raised. However, this band still appears as
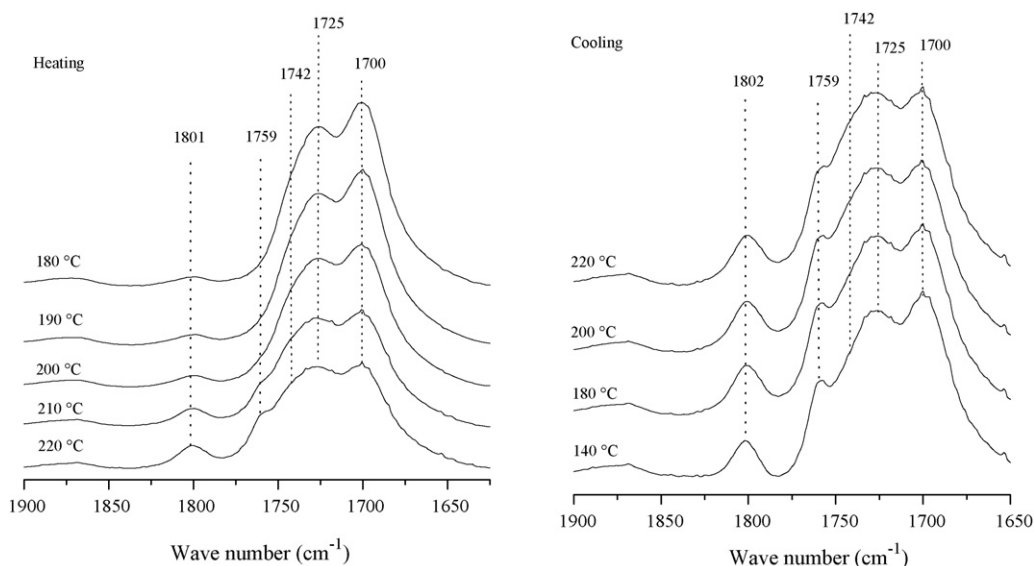

Fig. 6. FTIR spectra of IBM4VP-20/SMA-29 (15/85) at different temperatures, on heating and on cooling.
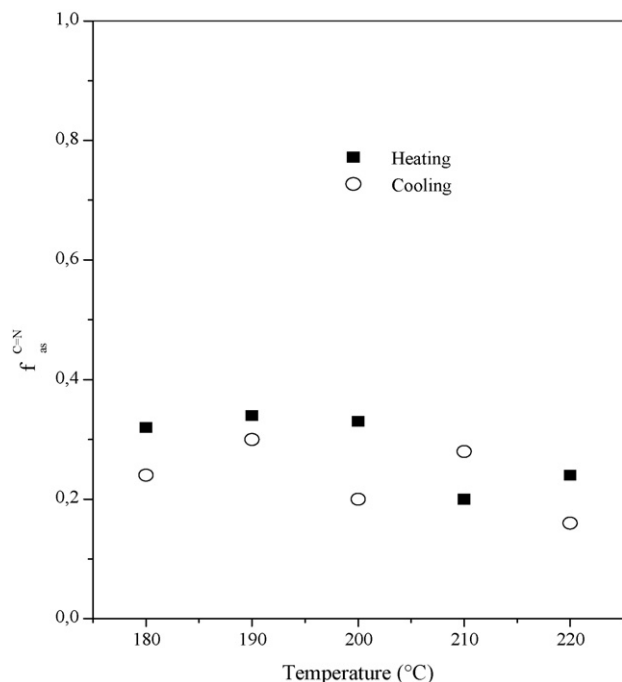
Fig. 7. Evolution of the fraction of the associated pyridine groups in the SMA-29/IBM4VP-20 (85/15) blend with temperature on heating and cooling in the range 1620–1570 cm^{-1}.

an observable shoulder even at 220 °C, suggesting a relative stability of these interactions. Indeed the fraction of the associated pyridine decreases progressively and leveled off as temperature is raised. Such results are in agreement with the increase of intensity of the bands characteristic of the anhydrides.

Based on these results, glass transition temperatures of some of these blends cast from THF were determined and found to behave negatively from the weight average of the T_g of the constituents. These lower T_g due to the known solvent effect [17] allow grater motion in the blend and enhance the anhydride formation. In a similar way as with IBM4VP-20/SMA-12 blends, the T_g of these blends as precipitates from heptane were then determined. A single glass transition temperature is observed
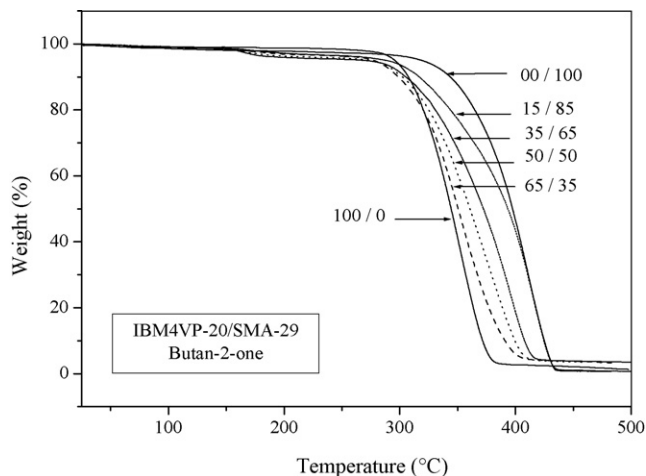

Fig. 8. Thermogravimetric curves of SMA-29 (0/100), IBM4VP-20 (100/0) and their complexes of different ratios.

with all these blends as shown in Fig. 2. The more positive deviation of the T_g of these IBM4VP-20/SMA-29 blends from the weight average of the constituents T_g's is mainly due to the presence of stronger and higher number of specific interactions that occurred between the carboxylic groups of the SMA-29 and the 4-vinylpyridine of the IBM4VP-20.

The intensity of these interactions, estimated from the Kwei constant q, shown in Fig. 2 indicates as expected that stronger polymer–polymer interactions occurred as characterized by a larger q value with a higher amount of carboxylic groups within the SMA-29 copolymer.

3.2.2. SMA-29/IBM4VP-20 interpolymer complexes

As it is seen from Fig. 8 the SMA29/IBM4VP20 complexes present a higher thermal stability than their homologous blends. The first degradation step occurs at higher temperature and with lower mass loss percentage compared with the corresponding blends. These results suggest that higher number of polymer–polymer interactions occurred between the copolymers when butan-2-one is the common solvent than within the
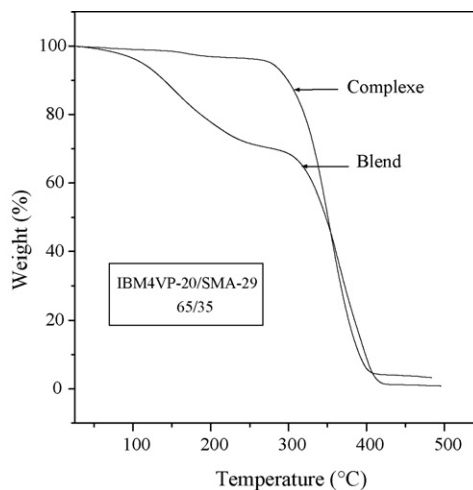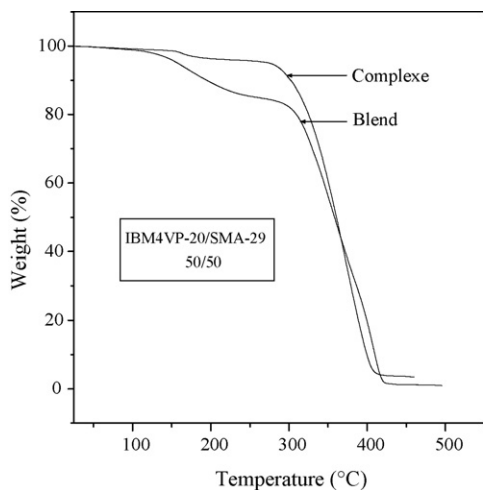

Fig. 9. Thermogravimetric curves of IBM4VP-20/SMA-29 blends and complexes of similar initial compositions.

Table 3
Thermogravimetric parameters of IBM4VP-20 (100/0), SMA-29 (0/100) and their complexes of their different ratios

Composition (%)	Stage 1		Stage 2		Stage 3		Residual weight (%) at 450 °C	T_g (°C)
	$T_2{}^a$	$M_2{}^b$	$T_3{}^a$	$M_3{}^b$	$T_4{}^a$	$M_4{}^b$		
00/100	288	97.0	–	–	440	0.90	0.833	156
15/85	150	99.0	260	96.2	420	0.82	0.689	143
35/65	150	98.5	260	95.0	420	3.50	3.803	142
50/50	132	98.8	262	95.5	415	3.60	3.913	137
65/35	152	98.5	250	97.7	423	4.08	3.485	120
100/00	256	98.2	–	–	352	2.80	2.424	86

[a] Temperatures of maximum degradation (°C).
[b] Residual weight in each stage (%).

corresponding blends cast from THF. These interpolymer interactions of hydrogen bonding types involve the carboxylic groups that must be dissociated before and delayed in this way the anhydride formation. Fig. 9 illustrates the significant differences observed with the thermogravimetric curves of blends and complexes of similar initial compositions. Table 3 gathers the data of the different steps of degradation and the T_g's of these complexes in a good agreement as those obtained as precipitates from heptane.

4. Conclusions

This contribution showed that depending on the density of methacrylic acid and 4-vinylpyridine, respectively, introduced within the polystyrene and poly(isobutyl methacrylate) matrices and the nature of the common solvent in which these two polymers are mixed, specific interactions of hydrogen bonding type occurred between the two copolymers as evidenced by FTIR and led to the formation of miscible blends or interpolymer complexes. The miscibility of the blends or interpolymer complexes is evidenced by DSC from the single T_g criterion. The positive Kwei q constant confirmed the presence of strong specific interactions. The interpolymer complexes obtained from butan-2-one exhibited higher thermal stability than their homologous blends cast from THF.

The FTIR study carried out above the glass transition temperature of the two constituents confirmed the presence of specific interactions of hydrogen bonding between these constituents and the formation of a fraction of anhydride within the (85/15) blend as cast from THF in the 180–220 °C temperature range. This is in agreement with the experimentally determined lower glass tran-

sition temperatures and enhanced degradation of these blends as compared to their corresponding interpolymer complexes. This study showed that among the aimed goals, only the thermal stability improvement and increase of T_g were achieved.

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