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Miscibility and Thermal Behaviour of Poly(styrene-*co*-itaconic acid)/Poly(butyl methacrylate-*co*-4-vinylpyridine) Mixtures. Accessibility and Self-Association Effects

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Summary: The miscibility and thermal behaviour of binary mixtures of poly(styrene-*co*-itaconic acid) containing 11 or 27 mol % of itaconic acid (PSIA-11 or PSIA27) with poly(butyl methacrylate) (PBMA)or poly(butyl methacrylate-*co*-4-vinylpyridine) containing 10 or 26 mol% of 4-vinylpyridine (PBM4VP-10, PBM4V-P26) were investigated by differential scanning calorimetry, scanning electron microscopy, FTIR spectroscopy and thermogravimetry. The results showed that 11 mol % of itaconic acid and 10 mol % of 4-vinylpyridine respectively introduced within the polystyrene and poly(butyl methacrylate) matrices induced the miscibility of this pair of polymers due to specific interactions of hydrogen bonding type with partial pyridine protonation that occurred between the two copolymers as evidenced by FTIR from the appearance of two new bands at 1607 cm^{-1} and 1640 cm^{-1}. Increasing itaconic acid content from 11 to 27 mol % led to a decrease of the intensity of the specific interactions within PSIA-27/PBM4VP blends and is attributed to both accessibility and self association effects as evidenced by DSC from the change of the shape of the Tg-composition curves and by FTIR spectroscopy. As shown from the thermogravimetric study, the presence of these specific interactions delayed the anhydride formation and improved the thermal stability of the blends.

Keywords: DSC; FTIR; poly(butyl methecrylate-*co*-4-vinylpyridine); poly (styrene-*co*-itaconicacid); thermal behaviour

Introduction

It has been reported in the literature that poly(butyl methacrylate) (PBMA) of a glass transition temperature Tg of about 30 °C, known like other poly(alkyl methacrylates) for its relatively low thermal stability, is immiscible with polystyrene (PS). The formation of a miscible PBMA/PS blend requires the presence of sufficient specific interactions between these two polymers. The introduction of increasing amount of methacrylic acid or acrylic acid (up to 29 mol %) within the polystyrene matrix so that interactions would occur between the ester groups of PBMA and the carboxylic groups of the acidic copolymer, was not sufficient to induce their miscibility.[1–2] The same acidic copolymers were however miscible with poly(ethyl methacrylate).[3] As also reported by Goh et al.,[4] the presence of bulky side groups inhibits the formation of such specific interpolymer interactions. In addition, not all the specific groups introduced within the polymer chains of a blend will be involved in intermolecular hydrogen bonding as chain

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rigidity affects the accessibility of the interacting sites. Moreover, several studies showed that the accessibility of functional groups to form specific interpolymer interactions in a polymer blend increases when the interacting species are adequately spaced out within the polymer chain.[5–7] The acidity and the strong self-association hydrogen bonds of the proton-donor component and the basicity of the proton-acceptor are also other factors that influence on the inter-association interactions.[8]

Miscible blends and interpolymer complexes were obtained when copolymers of PBM4VP were mixed with poly(styrene-co-methacrylic acid).[9] It is interesting to substitute methacrylic acid with itaconic acid which is expected due its two carboxylic groups to develop specific interactions with acceptors. Among the limited studies using itaconic acid, J.Filipovic et al.[10] reported very recently on the formation of interpolymer complexes of poly(itaconic acid) and poly(acrylamide) and their improved thermal stability as compared to that of poly(itaconic acid).

As an extension of our previous studies on miscibility of pair of polymers,[11–12] we have in the present contribution investigated the miscibility and thermal behaviour of binary mixtures of poly(styrene-*co*-itaconic acid) containing 11 or 27 mol % of itaconic acid with poly(butyl methacrylate-*co*-4-vinylpyridine) containing 10, 26 mol % of 4-vinylpyridine (PBM4VP-10 or PBM4VP-26) as blends by differential scanning calorimetry, scanning electron microscopy and by FTIR spectroscopy. Both accessibility and self association effects on the miscibility and thermal stability of these blends will be discussed.

Experimental Part

Materials

Poly(butyl methacrylate) (PBMA) and random copolymers of poly(butyl methacrylate-*co*-4-vinylpyridine) containing 10 or 26 mol % of 4-vinylpyridine (PBM4VP-10 or PBM4VP-26,) and poly(styrene-*co*-itaconic acid) containing 11 or 27 mol % of itaconic acid) (PSIA-11 or PSIA-27) 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 repeated dissolution/reprecipitation cycles and dried under vacuum at 50 °C for several days.

Characterizations

The styrene and 4-vinylpyridine contents in the PSIA and PBM4VP copolymers were determined by UV spectroscopy. Average molecular weights $\overline{Mw}$ and polydispersity indices (I) of these copolymers were determined by GPC using a Schimadzu CTO-10 AVP chromatograph equipped with a refractive index detector, calibrated with polystyrene standards. The $\overline{Mw}$ PSIA copolymers were however determined using the same standards and DMF as the solvent. These $\overline{Mw}$ seem to be over estimated. Similar results are reported in the literature.[13] The results of these characterizations and the glass transition temperature of these copolymers obtained by DSC traces are summarized in Table 1.

Qualitative Tests

PSIA-11, PSIA-27 and PBM4VP copolymers were separately dissolved in THF to form dilute solutions. Appropriate amounts of acidic (PSIA-11 or PSIA-27) and basic (PBM4VP-10 or PBM4VP-26) solutions

Table 1.
Characteristics of polymers.

Polymers	Copolymers IA	Composition mol % 4VP	$\overline{Mw}$ (g/mol)	$\overline{Mn}$ (g/mol)	$I=\overline{Mw}/\overline{Mn}$	Tg (°C)
PBMA	0	0	705785	538461	1.31	30
PBM4VP-10	0	10.6	343921	190476	1.80	38
PBM4VP-26	0	26.0	301594	156587	1.92	51
PSIA-11	11.31	0	3136778	1508616	2.07	71
PSIA-27	26.66	0	2210979	1036828	2.13	91

were mixed together by drop wise addition of PSIA solution to PBM4VP solution. Since the refractive indices of the two copolymers are different, a visual observation of one homogeneous phase with each ternary mixture of these copolymers and THF is a preliminary evidence of their miscibility. Transparent films were also observed after evaporation of the solvent.

Thermal Analysis

Films of the different copolymers and of blends of PSIA-11 or PSIA-27 with each of PBMA, PBM4VP-10 and PBM4VP-26 were prepared from THF solutions .These films, dried to constant weight in a vacuum oven at 40 °C during several days to remove traces of solvent, were used in the thermal analysis.

Thermogravimetric analysis was carried out prior to DSC on a TA instruments TGA-Q500 under nitrogen atmosphere from 40 °C to 500 °C at a heating rate of 10 °C/min.

The glass transition temperatures Tg of these copolymers and of their blends were measured using a Perkin Elmer DSC-7 at a heating rate of 20 °C/min under a nitrogen atmosphere in the –20 °C to 140 °C temperature range based on TGA analysis that indicates their thermal stability in this temperature range. The Tg 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.

FTIR Measurements

Thin films of the PSIA-11 and its blends of different ratios with PBM4VP copolymers of different amount of 4-vinylpyridine were prepared from dilute solution in THF. The films were kept in a vacuum oven for several days at 50 °C until the solvent was removed .The FTIR/ATR spectra were recorded at room temperature with Vertex 70 spectrometer using 60 scans at a resolution of 2 cm^{-1}.

SEM Observations

SEM was used to evaluate the phase morphology of the binary blends. Blends were immersed in liquid nitrogen, fractured, and coated with gold before microscopy. A PHILPS XL30 scanning electron microscope with a voltage of 10 KV, was used to observe the sample surface.

Results and Discussion

PSIA/PBMA Blends

Qualitative tests carried out on these blends showed that depending on the blend composition homogeneous or heterogeneous phases are observed when PSIA-11 or PSIA-27 is mixed with PBMA in THF. This may be considered as a preliminary evidence of their partial miscibility.

Based on the carried out preliminary thermal stability results, a DSC analysis was performed to study the phase behaviour of these blends in the –20 to 140 °C temperature range. The immiscibility of these blends is confirmed from the observation of two glass transition temperatures (Figure 1). Though a single Tg is observed with blends containing an excess of PSIA which may bay be considered as the main polymeric matrix, an increasing compatibilization is observed,in agreement with the observed scanning electron microscopy results..This may be due to the presence of some specific interactions that occurred between the itaconic acid groups of the PSIA and the ester groups of PBMA.

These results are in agreement with those obtained by scanning electron microscopy. (Figure 2) illustrates as an example the micrographs of the (30/70) (50/50) PSIA-11/PBMA blends that confirm the phase separation of the two components of the blend and that of (90/10) blend showing a fine dispersion of the PBMA in the matrix.

Similar behaviour is observed with blends of PSIA-27/PBMA. Blends containing up to 70% by weight of PSIA-27 displayed two Tg confirming their immiscibility. Self-association of carboxylic groups is expected to increase within the PSIA-27 as compared to PSIA-11 and compete with the specific interpolymer interactions that would enhance the

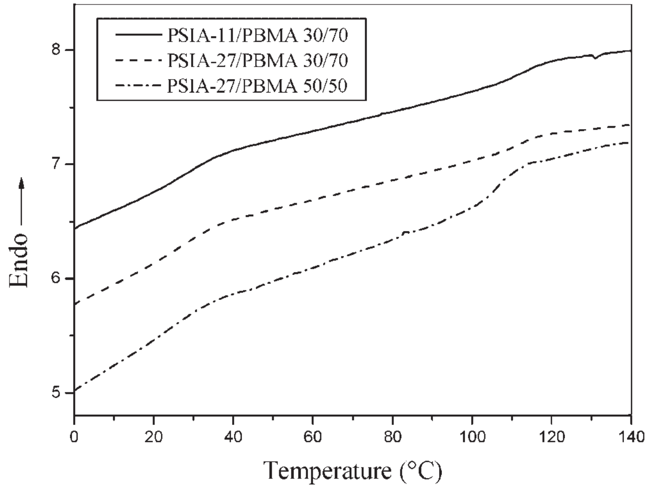

Figure 1.
DSC thermograms of PSIA-11/PBMA and PSIA-27/PBMA blends.

miscibility of the blends. This reduces the miscibility window of the PSIA27/PBMA system.

PSIA/PBM4VP Blends

Thermal Analysis

The introduction of small amount of 4-vinylpyridine as low as 10 mol % within the PBM4VP copolymers was sufficient to induce the miscibility of the blends above over the entire composition range. In addition to the relatively weak itaconic acid-butyl ester interactions, the preferentially pyridine-itaconic acid interactions overcame the steric hindrance of the butyl groups and induced the miscibility of the different PSIA-11/PBM4VP blends in the

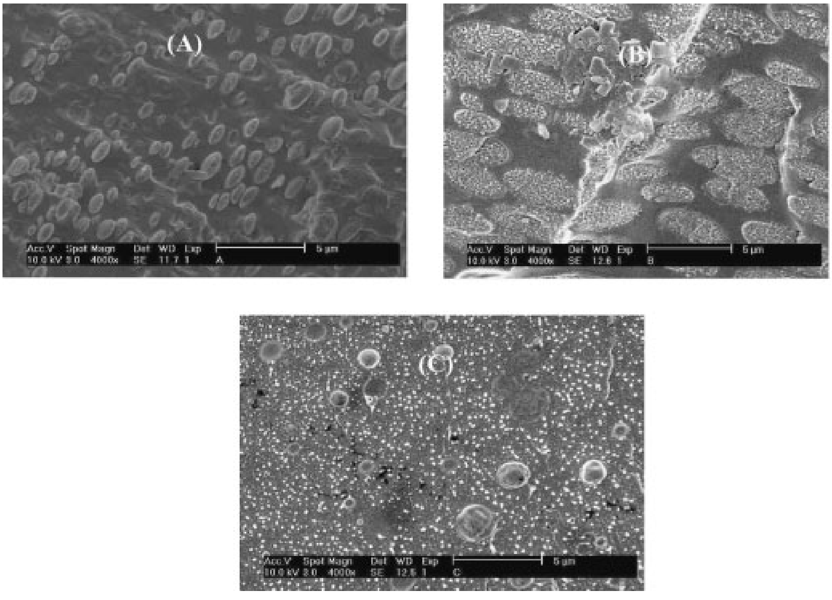

Figure 2.
SEM micrograph of PSIA-11/PBMA of different ratios, A (30/70), B (50/50), C (90/10).

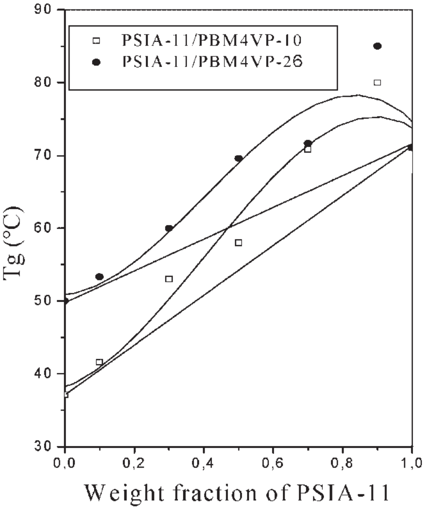

Figure 3.

Glass transition temperature (Tg) of PSIA-11/PBM4VP-10 and PSIA-11/PBM4VP-26 blends, as a function of PSIA-11 content.

whole composition range. Indeed a single compositionally dependent glass transition temperature is observed with all the studied PSIA11-/PBM4VP-10 and PSIA-11/PBM4VP-26 blends.

As shown in (Figure 3), the Tg of these blends deviate positively from the weight average of the constituents Tgs. The deviation is even more important with blends containing an excess of PSIA-11.This is due to the presence of strong specific interactions that occurred between the carboxylic groups of the PSIA-11 and the 4-vinylpyridine and eventual ester groups of the PBM4VP. Since the interactions between ester and carboxylic groups are weak, the miscibility of PSIA-11/PBM4VP 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[14]:

$$Tg_b = [(W_1 \cdot Tg_1 + kW_2 Tg_2)/(W_1 + kW_2)] + qW_1W_2 \qquad (1)$$

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

For miscible blends, we can assume $k = 1$, the deduced q values indicate that strong interactions occurred between the two constituents of the blend. The simplified equation is:

$$Tg_b = W_1 Tg_1 + W_2 Tg_2 + qW_1W_2 \qquad (1')$$

Tg_b, Tg_1, Tg_2: glass transition temperature of blend and their component 1 and 2.

W_1, W_2: Weight fraction of polymers 1 and 2 of the blend.

q: measures the strength of specific interactions between two polymers of the blend.

The obtained q values for the PSIA-11/PBM4VP-10 and PSIA-11/PBM4VP-26 systems were of 22,96 and 24,53 respectively.

The miscibility of these blends was also analyzed using the Schneider approach[15] given by the equation below:

$$(Tg_b - Tg_1)/(Tg_2 - Tg_1)W_{2C} = (1 + K_1) - (K_1 + K_2)W_{2C} + K_2\, W_{2C}^2 \qquad (2)$$

Where the corrected weight fraction of the component of highest Tg (PSIA-11) is given by:

$$W_{2C} = KW_2/(W_1 + KW_2) \quad \text{and} \quad K = \rho_1\, Tg_1/\rho_2\, Tg_2 \qquad (3)$$

With: W_1, W_2, Tg_1, Tg_2, ρ_1, ρ_2 the weight fractions, glass transition temperatures and densities of constituents 1 and 2 of the blends.

The results confirm once more the presence of strong specific interactions as illustrated in (Figure 4) that shows plots of $(Tg_b - Tg_2)/(Tg_2 - Tg_1)\ W_{2C}$ versus W_{2C} for the different miscible blends.

When PSIA-27 is mixed together with basic copolymers of increasing 4-vinylpyridine content (PBM4VP-10, PBM4VP-26 and) in 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. Increasing the

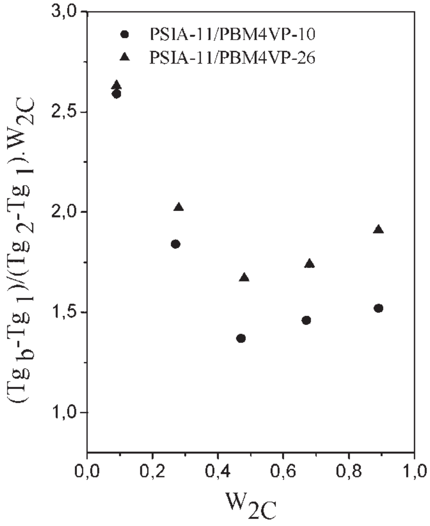

Figure 4.
$(Tg_b - Tg_1)/(Tg_2 - Tg_1)$ W_{2C} versus W_{2C} for PSIA-11/PBM4VP-10 and PSIA-11/PBM4VP-26 blends.

itaconic acid content from 11 to 27 mol % showed that all the PSIA-27/PBM4VP-10, PSIA-27/PBM4VP-26 blends of different ratios are miscible since a single Tg is observed with each blend. The Tg-composition behaviour of these latter blends is however different from that of the systems above. S shaped curves (Figure 5) with these various blend systems. Such behaviour may be interpreted in terms of different types of interactions due to the presence of a higher number of self-associated itaconic acid within the PSIA-27 that are not all accessible and that will limit the number of specific interpolymer interactions. Both the dilution of the itaconic acid within the polystyrene matrix and the self-association effects are evidenced (Figure 6), that shows significant difference when PSIA-11/PBM4VP system are compared to PSIA-27/PBM4VP.

FTIR Spectroscopy

We have used FTIR spectroscopy, a well known and powerful technique to study the specific interactions that occurred between the carboxylic groups of the PSIA-11 and the pyridine nitrogen atom of the different PBM4VP copolymers within the blends. The spectrum of PSIA-11 shows in the 3600–2400 cm^{-1} region a broad band centred around 3200 cm^{-1} and a satellite band at 2630 cm^{-1}. In the carbonyl 1780–1660 cm^{-1} region, two bands attributed to free and to the different self-associated carboxylic acid groups are respectively observed at 1742 cm^{-1} and 1706 cm^{-1}, though this copolymer possesses two different carboxylic

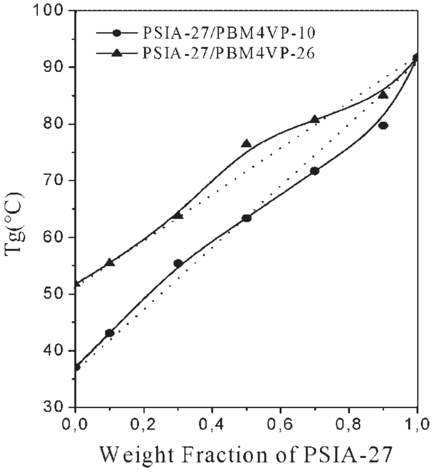

Figure 5.
Glass transition temperature (Tg) of PSIA-27/PBM4VP-10 and PSIA-27/PBM4VP-26 blends, as a function of PSIA-27 content.

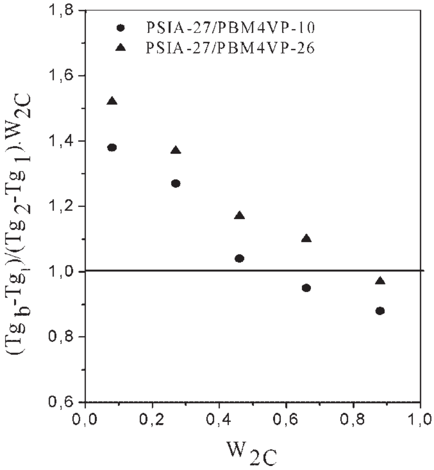

Figure 6.
$(Tg_b - Tg_2)/(Tg_2 - Tg_1)$ W_{2C} versus W_{2C} for PSIA-27/PBM4VP-10 and PSIA-27/PBM4VP-26 blends.

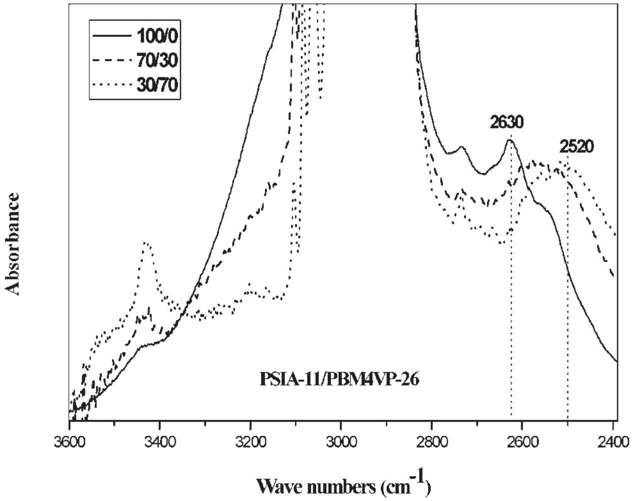

Figure 7.
FTIR spectra of PSIA-11 and PSIA-11/PBM4VP-26 blends in 3600–2400 region.

groups. The PBM4VP copolymer absorbs strongly in the carbonyl region around 1726 cm^{-1} and in the pyridine ring 1650–1550 cm^{-1} region at 1597 cm^{-1}.

Changes are observed in these regions when PSIA-11 is added to the different basic PBM4VP copolymers. Depending on its content in the blend composition, the PSIA-11 acidic copolymer may interact at the two sites of the basic copolymer.

The broad bands in 3600–2400 cm^{-1} of the PSIA-11 are affected by the progressive addition of the basic PBM4VP copolymer (Figure 7). The intensity of the band at 3200 cm^{-1} decreases,while a broadening and an important shift to lower wave numbers up to 2520 cm^{-1} are observed with the satellite band initially centred at 2630 cm^{-1}.This is due to the dissociation of some of the dimers and their replacement by interactions between the constituents of different nature within the blends. The overlap of the different contributions from the two copolymers in the carbonyl region makes it difficult to investigate directly the interactions in this region.

The interpolymer interactions that occurred between the two copolymers within the different blend systems were also investigated in the 1650–1550 cm^{-1} pyridine ring region. Though the free pyridine band located at 1597 cm^{-1} overlaps with styrene rings observed at 1601 cm^{-1}, significant changes occurred upon mixing PSIA-11 with each of the different PBM4VP copolymers. As it is shown in (Figure 8), this band broadens and shifts to higher wave numbers with increasing intensity as the PSIA-11content increases in the blend. This shift of about 10 cm^{-1} for blends containing

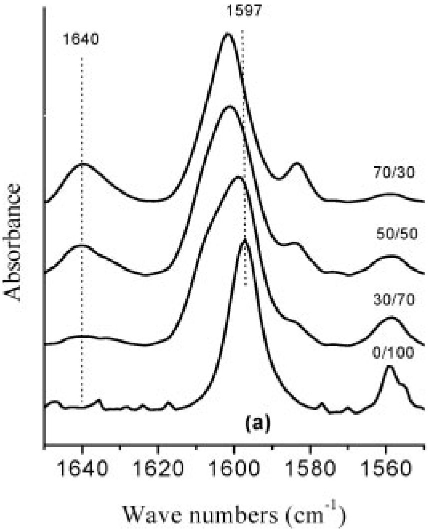

Figure 8.
FTIR spectra of PSIA-11/PBM4VP-26 blends in pyridine ring (a).

less than 50% by weight of PBM4VP becomes even larger when the PSIA-11 is an excess. In addition, a small peak attributed to a partial pyridine nitrogen protonation is observed around 1640 cm^{-1}.

This indicates that stronger interactions occurred particularly when the PSIA-11 is in excess and that both hydrogen bonding and partial ionic interactions occurred. The self-association and dilution effects are evidenced from (Figure 9) that illustrates the 1:1 ratio spectra of PSIA-11/PBM4VP-10, PSIA-11/PBM4VP-26 and PSIA-27/PBM4VP-26 blends from which the polystyrene contribution is subtracted .Indeed, the fraction of free pyridine decreases with dilution of the interacting species within the polymer matrices resulting in stronger specific interpolymer interactions.

Such observations confirm the DSC results that showed an important deviation in the Tg-composition of the different PSIA11/PBM4VP blend systems.

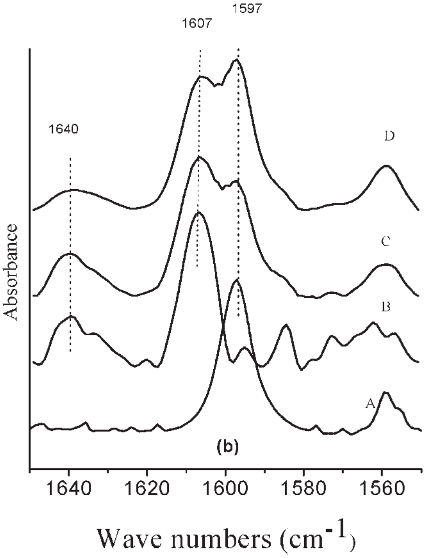

Figure 9.
FTIR spectra subtracting PS, of PBM4VP-26 (**A**), and 50/50 ratio of PSIA-11/PBM4VP10 (**B**), PSIA-11/PBM4VP-26 (**C**) and PSIA-27/PBM4VP-26 (**D**) (b).

Thermogravimetric Analysis
(Figure 10) illustrates the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the PSIA-11, PBM4VP-26 copolymers and of their blends of different ratios. Two stages of degradation are depicted with the PSIA-11 copolymer. The first stage of 11,91% weight loss, in the 102–242°C temperature range with two maxima at 155 °C and 197 °C, is assigned to moisture absorption by the hydrophilic groups of the PSIA-11 and the formation of traces of anhydrides .The second step of degradation that occurs between 330 °C and 453 °C with a T_{max} of 416 °C corresponds to the degradation of the main chain.

The degradation of PBM4VP-26 occurs mainly through a single step between 257 °C and 402 °C with a T_{max}= 336 °C.

The thermogravimetric parameters for this PSIA-11/PBM4VP-26 system depend

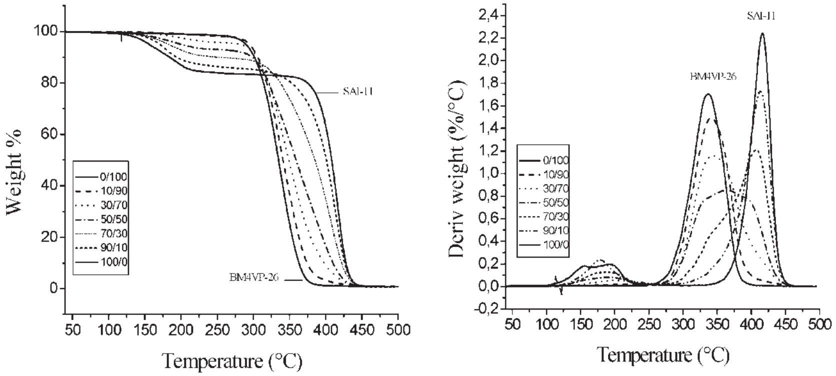

Figure 10.
Thermogravimertic TGA and derivative thermogravimetric DTGA curves of PSIA-11/PBM4VP-26 of different ratios.

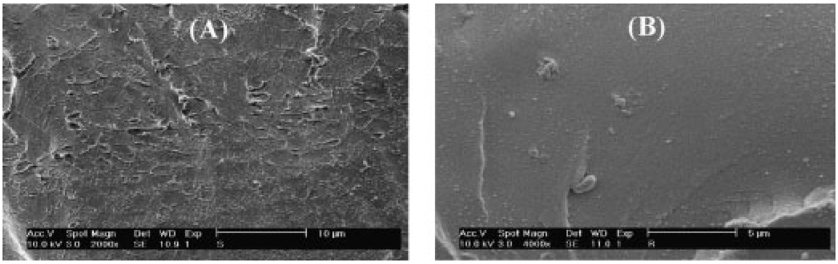

Figure 11.
SEM micrograph of PSIA-11/PBM4VP26 of different ratios A (30/70), B (50/50).

on the composition of the blend. The first stage of degradation of these blends shows a tendency towards a decrease of the amount of absorbed water from the observation of only one peak shifting to higher temperature as the fraction of PBM4VP increases in the blend. This is due to the presence of specific interactions that occurred between the itaconic acid and the pyridine groups that delayed the anhydride formation.

The DTG curves of the blends show a broad second degradation stage between 250 °C and 450 °C with a T_{max}, attributed to the decomposition of the major copolymer in the blend and another loss step, not well resolved,due to the degradation of the minor component of the blend .The peak at low temperature is characteristic of the main chain degradation of PBM4VP-26.This peak shifts to a higher temperature when PSIA-11 content increases in the blend. This is an indication of an increase of thermal stability.

SEM

The miscibility of these blends is also evidenced at a microscopic scale by SEM as shown in (Figure 11) that illustrates the micrographs of some of the PSIA-11/PBM4VP-26 blends showing a fine dispersion of the component in the matrix.

Conclusion

This contribution showed that densities as low as 11 mol % of itaconic acid and 10 mol % of 4-vinylpyridine respectively introduced within polystyrene and poly(butyl methacrylate) matrices were sufficient to overcome the steric hindrance of the butyl groups and induce the miscibility of this pair of polymers. This is mainly due to specific interactions of hydrogen bonding type with partial pyridine protonation that occurred between the two copolymers as evidenced by FTIR from the appearance of new bands at 1607 cm^{-1} and 1640 cm^{-1} attributed to hydrogen bonding and protonated pyridine respectively and by DSC from the positive deviation of the Tg-composition curves. Miscible blends were still observed when itaconic acid content increased from 11 to 27 mol % within the polystyrene matrix. However, a decrease of the intensity of the specific interactions within PSIA-27/PBM4VP blends attributed to both accessibility and self association effects is evidenced by DSC from the change of the shape of the Tg-composition curves and by FTIR spectroscopy. The TGA analysis shows that specific interactions delayed the degradation of PBM4VP-26

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