Thermochimica Acta 483 (2009) 49–54

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Miscibility and phase behaviour of binary and ternary homoblends of poly(styrene-*co*-acrylic acid), poly(styrene-*co*-*N*,*N*-dimethylacrylamide) and poly(styrene-*co*-4-vinylpyridine)

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ARTICLE INFO

Article history:
Received 29 July 2008
Received in revised form 2 November 2008
Accepted 6 November 2008
Available online 17 November 2008

Keywords:
Miscibility
Phase behaviour
Poly(styrene-*co*-acrylic acid)
Poly(styrene-*co*-*N*,*N*-dimethylacrylamide)
Poly(styrene-*co*-4-vinylpyridine)
Ternary homoblend

ABSTRACT

The miscibility and phase behaviour of binary and ternary homoblends prepared from poly(styrene-*co*-acrylic acid) (SAA14), poly(styrene-*co*-*N*,*N*-dimethylacrylamide) (SAD25) and poly(styrene-*co*-4-vinylpyridine) (S4VP15) were investigated by DSC.

SAA14 is miscible with both S4VP15 and SAD25 and interacts more strongly with S4VP15 than with SAD25 as evidenced by comparing their compositional variation of glass transition temperatures (T_g). Positive and negative deviations from linear average line were respectively observed with the SAA14/S4VP15 and SAA14/SAD25 blends.

Several conventional theoretical approaches were used to describe these T_g-composition behaviours. The one parameter Gordon–Taylor equation or the two parameters Kwei equation describe very well the behaviour of SAA14/S4VP15 system. However, the recent three parameters Brostow equation was needed to reproduce experimental T_g-composition for the SAA14/SAD25 system.

Reasonable agreement with the experimental values are obtained for both systems when the fitting parameter free method developed by Coleman et al. is applied to predict the composition dependence of the glass transition temperature.

The experimental phase diagram of the SAA14/S4VP15/SAD25 ternary polymer blend system presents an immiscibility region due to the unbalanced interactions among the three polymer pairs.

1. Introduction

Styrene polymers are among the largely used and most recycled materials and as many others such as PVC, PPE or PC, they are rarely used as unmodified resins and often require blending to provide more economic materials with specific properties and improved processability.

It is however well known that most polymer pairs are immiscible because the entropy of mixing polymers is usually small and that the introduction of specific interactions of hydrogen bonding type between the two constituents of the blend is now a method used to enhance their miscibility [1–4]. Though increasing number of binary miscible blends are now reported in the literature [5–8], multicomponent polymer systems have received less attention because of the difficulties encountered in their compatibilization. Yet, combining different polymers with the help of a compatibilizer could be a very interesting way to develop high performance materials.

It is rather rare to find a single phase ternary polymer blends in the whole composition range. Even in the case of ternary systems composed of three miscible polymer pairs, few ternary polymer blends have been reported to be miscible over the full composition range [9–11], only in limited cases where the physical $\Delta\chi$ and interactionel ΔK effects are negligible or finely balanced. An unusual completely miscible ternary blend of phenolic/phenoxy/PCL was however recently reported [12].

Several studies reported [13–15] that some ternary blends composed of three miscible binary blends showed a closed immiscibility loop phase diagram.

In the present study, we have investigated by DSC and several conventional theoretical approaches including that of Coleman and co-workers [16] and the one very recently proposed by Brostow et al. [17] the specific interactions, previously evidenced by FTIR [18], that occurred within binary homoblends of different ratios prepared from poly(styrene-*co*-acrylic acid) containing 14 mol% of acrylic acid (SAA14), poly(styrene-*co*-*N*,*N*-dimethylacrylamide)

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doi:10.1016/j.tca.2008.11.001

Table 1
Polymer characteristics.

Copolymer	Styrene content (mol%)	M_W (kg/mol)	M_W/M_N	T_g (°C)	T at 10% weight loss (°C)	T at maximum weight loss (°C)
SAA14	86^{NMR}	59.7	2.67	119	376	430
S4VP15	$85^{UV,NMR}$	6.6	2.98	104	342	392
SAD25	75^{UV}	10.7	3.50	98	350	411

M_w: mean weight molecular weight, M_W/M_N: polydispersity index, T_g: glass transition temperature

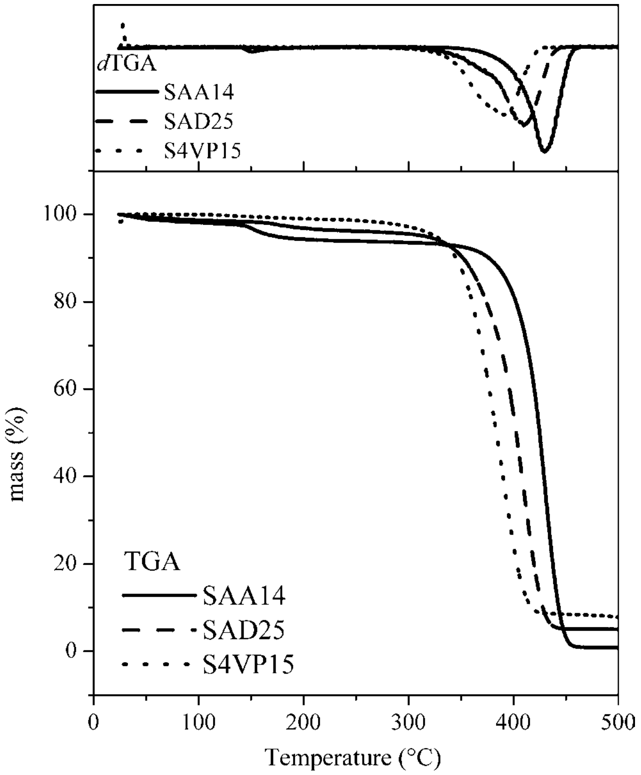

Fig. 1. TGA (bottom) and *d*TGA (top) of SAA14, SAD25 and S4VP15 copolymers.

containing 25 mol% of *N*,*N*-dimethylacrylamide (SAD25) and poly(styrene-*co*-4-vinylpyridine) containing 15 mol% of 4-vinylpyridine.

The phase behaviour of the binary homoblends and ternary blends of these three copolymers, based on similar polymer matrix, in which SAA14 interacts with different strength with each of S4VP15 and SAD25, is also examined.

2. Experimental

2.1. Synthesis and characterization of copolymers

Poly(styrene-*co*-acrylic acid) containing 14 mol% of acrylic acid (SAA14), poly(styrene-*co*-4-vinylpyridine) containing 15 mol% of 4-vinylpyridine (S4VP15) and poly(styrene-*co*-*N*,*N*-dimethylacrylamide) containing 25 mol% of *N*,*N*-dimethylacrylamide (SAD25), were prepared by free radical polymerization using azo-bis-isobutyronitrile as initiator at 60 °C and characterized in a similar way as previously described [19] by UV spectroscopy and proton NMR. The average molecular weights of these copolymers were determined by GPC using a HP 1100 HPLC. The copolymer characteristics are listed in Table 1.

2.2. Thermal analyses

The thermal stability of the as-cast copolymers was checked by TGA using a Mettler Toledo 851^e at a heating rate of 10 °C/min under nitrogen flow. These copolymers showed different temperatures of degradation compared to polystyrene and were stable up to 350 °C, as displayed from their TGA and *d*TGA curves in Fig. 1.

Copolymer or copolymer blend films were cast from THF solutions and dried at room temperature before they were kept under reduced pressure in a vacuum oven at 60 °C for several days prior to use. The glass transition temperature T_g of these copolymers and of their binary and ternary blends of different ratios was measured

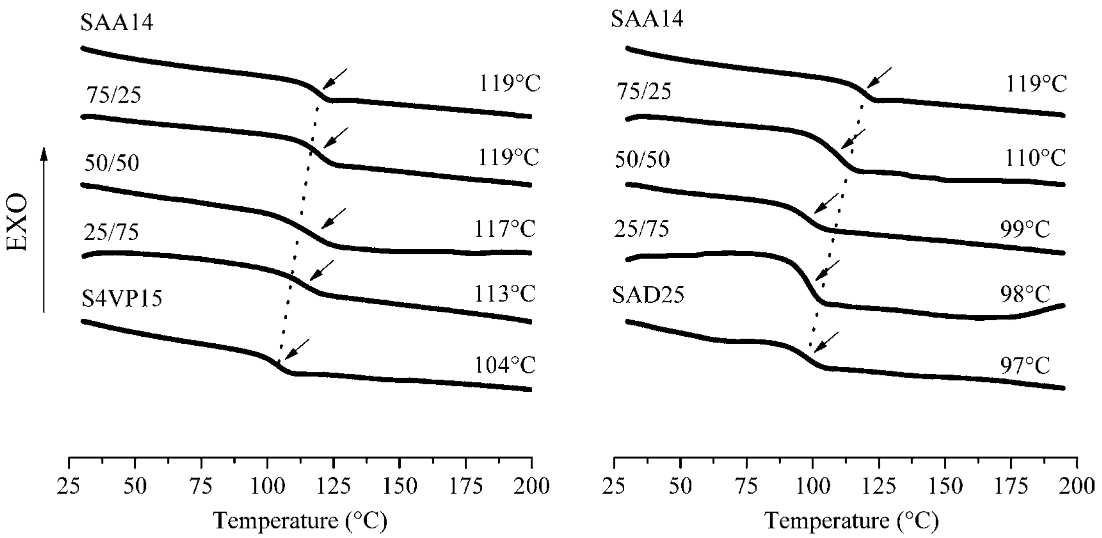

Fig. 2. DSC thermograms of SAA14/S4VP15 (left) and SAA14/SAD25 (right) binary blend systems.

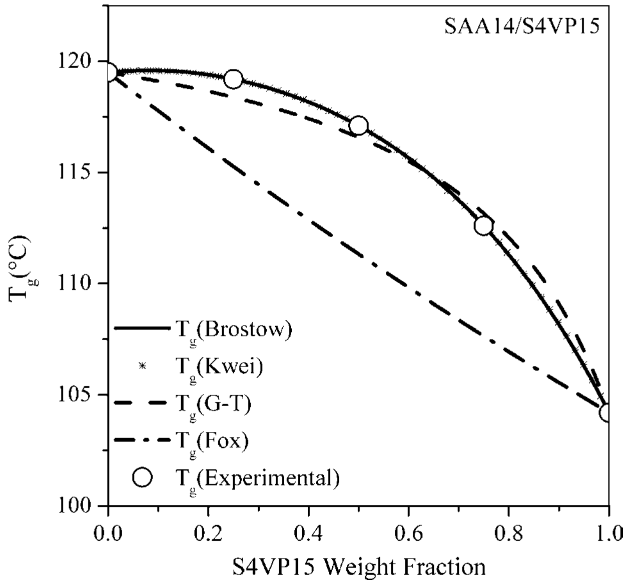

Fig. 3. T_g-composition of the SAA14/S4VP15 binary blend system.

using Mettler Toledo 821^e DSC, at a heating rate of 20 °C/min under nitrogen flow. All the thermograms recorded during the second heating scan were considered to obtain the T_g values.

3. Results and discussion

3.1. Thermal analyses of binary blends

The T_g of a polymer is an important characteristic that affects its final properties and potential applications. We have carried out a DSC analysis for the copolymers, three SAA14/S4VP15, SAA14/SAD25, S4VP15/SAD25 binary blends and SAA14/S4VP15/SAD25 ternary blend. Fig. 2 shows DSC thermograms of SAA14/S4VP15 and SAA14/SAD25 blends of different ratios. A single glass transition temperature is observed with these systems over the whole composition range. This indicates their miscibility mainly due to the specific interactions that occurred between the carboxylic acid groups of SAA14 and the pyridine groups of S4VP15 or amide groups of SAD25 as evidenced qualitatively by FTIR spectroscopy [18].

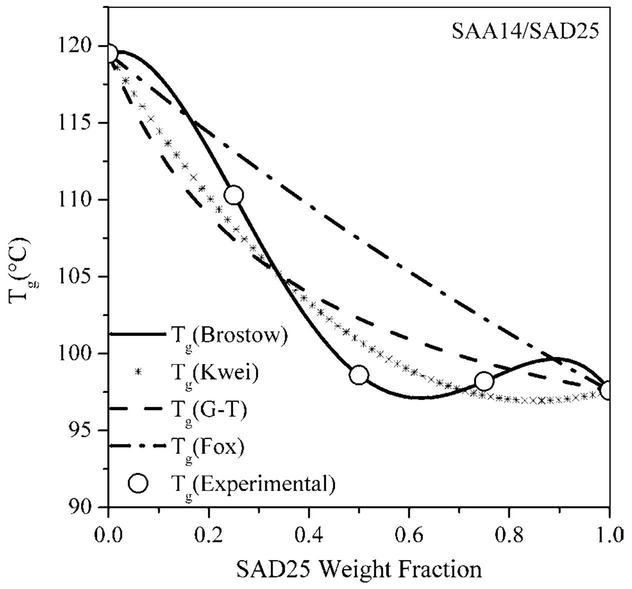

Fig. 4. T_g-composition of the SAA14/SAD25 binary blend system.

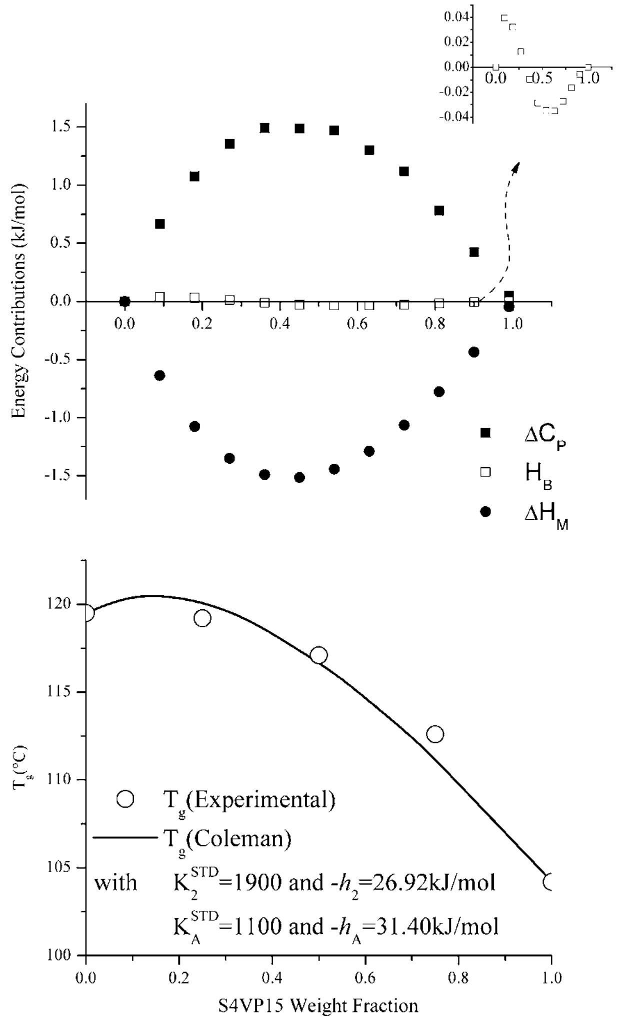

Fig. 5. Energy contributions to the T_g equation (top) and the predicted T_g of the SAA14/S4VP15 polymer blend system (bottom).

As it can be seen in Figs. 3 and 4, two different T_g-composition behaviours were observed with these systems. A positive deviation from linear average line is observed with SAA14/S4VP15 blends while a negative deviation is shown with SAA14/SAD25 system.

We have in a first step used the well-known Fox, Gordon–Taylor and Kwei approaches as well as the new equation proposed by Brostow et al. [17], to describe the composition dependence of T_g of these miscible blends from:

Fox equation:

$$\frac{1}{T_g}(\text{blend}) = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \tag{1}$$

Gordon–Taylor equation:

$$T_g(\text{blend}) = \frac{(w_1 T_{g,1} + K_{GT} w_2 T_{g,2})}{(w_1 + K_{GT} w_2)} \tag{2}$$

Kwei equation:

$$T_g(\text{blend}) = \frac{w_1 T_{g,1} + K_{\text{Kwei}} w_2 T_{g,2}}{w_1 + K_{\text{Kwei}} w_2} + q w_1 w_2 \tag{3}$$

Brostow equation:

$$\begin{aligned} T_g(\text{blend}) &= w_1 T_{g,1} + (1 - w_1) T_{g,2} + w_1 (1 - w_1)\,[a_0 + a_1(2w_1 - 1) \\ &\quad + a_2(2w_1 - 1)^2 + a_3(2w_1 - 1)^3] \end{aligned} \tag{4}$$

Table 2
Fitting parameters using equations of Gordon–Taylor, Kwei and Brostow.

Polymer blend system	GT	Kwei	Brostow
SAA14/S4VP15	$K_{GT} = 4.24$	$K_{Kwei} = 2.44$; $q = 8.20$	$a_0 = 21.00$; $a_1 = 5.60$; $a_2 = 2.40$
SAA14/SAD25	$K_{GT} = 0.27$	$K_{Kwei} = 0.99$; $q = -30.86$	$a_0 = -39.80$; $a_1 = -6.13$; $a_2 = 67.46$

where $T_{g,1\text{ or }2}$ and $w_{1\text{ or }2}$ are the glass transition temperatures of the pure components and their corresponding weight fractions, respectively. K_{GT}, K_{Kwei}, q, and a_i are adjustable parameters determined from experimental T_g-composition curves and are gathered in Table 2.

The positive value of q and the relatively high value of K_{GT} (larger than 1) indicate that strong interactions occurred within the SAA14/S4VP15 blends between the carboxylic and the pyridine groups.

Higher constants previously obtained with the same basic copolymer S4VP15 and poly(styrene-*co*-methacrylic acid) containing 15 mol% of methacrylic acid ($q = 70$) indicate that stronger interactions occurred within this latter system[19].

Weaker interactions, characterized by a negative q value and a Gordon–Taylor K_{GT} constant less than 1, occurred between SAA14 and SAD25. The results are in good agreement with those previously obtained by FTIR spectroscopy that confirmed that stronger interactions occurred between SAA14 and S4VP15 than between SAA14 and SAD25 [18].

Using the equation of Brostow, three terms were sufficient to obtain good fitting results which are quite better than those obtained for the Kwei equation. In the case of SAA14/S4VP15 system, the one parameter Gordon–Taylor equation or the two parameters Kwei equation describe very well the compositional behaviour of the T_g. However, the three parameters Brostow equation was needed to reproduce experimental T_g-composition for the SAA14/SAD25 system. So, this latter system seems to be more complex than the SAA14/S4VP15 as the complexity is measured by Eq. (4).

We have in a second step applied the fitting parameter free method developed by Coleman et al. [16] to predict the composition dependence of the glass transition temperature for both SAA14/S4VP15 and SAA14/SAD25 systems.

Accordingly, the derived T_g equation, presented below, is separated into three terms, a nonspecific interaction component, a term that accounts for that part of the temperature dependence of the specific heat that is due to self-association and a heat of mixing in

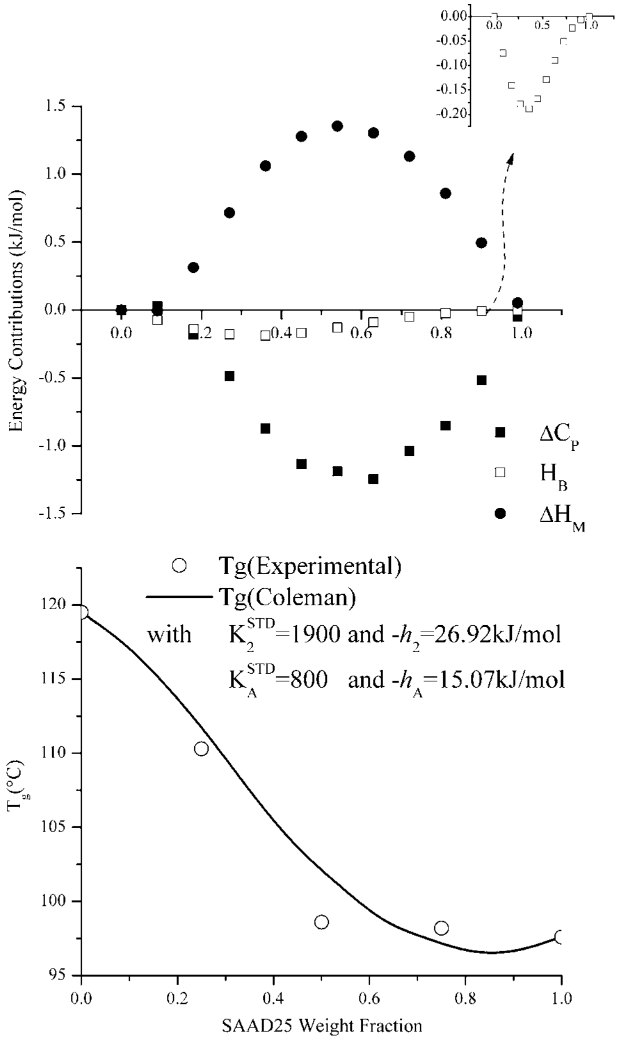

Fig. 6. Energy contributions to the T_g equation (top) and the predicted T_g of the SAA14/SAD25 polymer blend system (bottom).

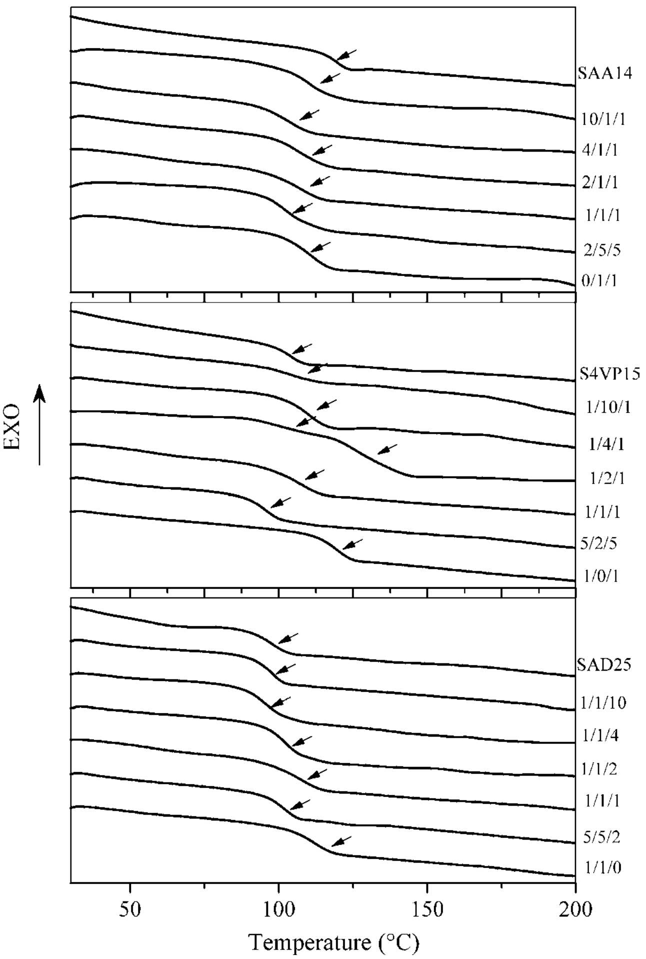

Fig. 7. Selected second scan DSC thermograms of SAA14/S4VP15/SAD25 ternary blends with various compositions.

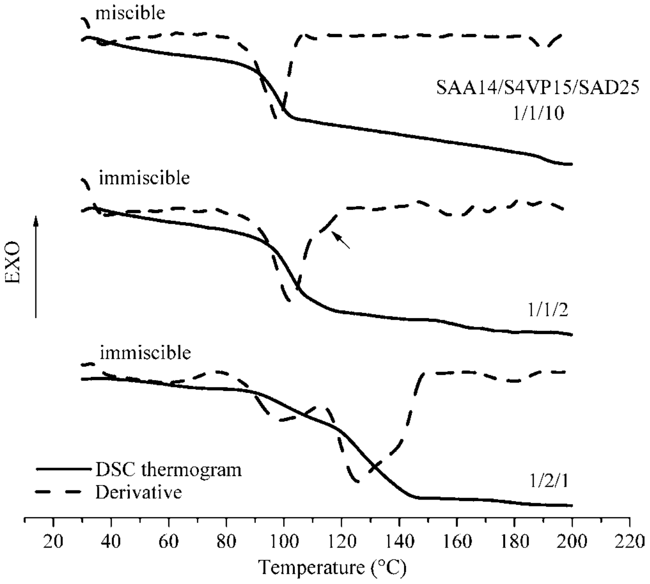

Fig. 8. Selected thermograms and their derivatives showing different behaviours.

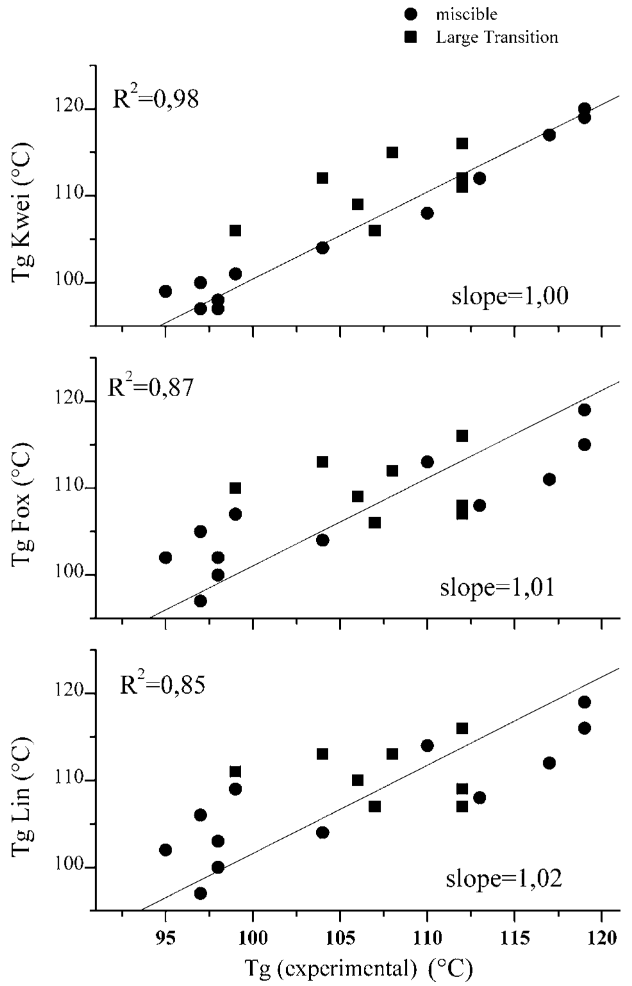

Fig. 9. T_g (predicted) vs. T_g (experimental) of SAA14/S4VP15/SAD25 ternary polymer blend.

the liquid state term:

$$[w_1\Delta C_{p,1}(T_g(\text{blend})-T_{g,1})+w_2\Delta C_{p,2}(T_g(\text{blend})-T_{g,2})] + w_2[(H_B)_{T_g(\text{blend})}-(H_B)_{T_{g,2}}]+\Delta H_M=0 \quad (5)$$

where $\Delta C_{p,i}$ is the discontinuity in the specific heat of the i component at the respective $T_{g,i}$. $(H_B)_{Tg}$ is the pure state enthalpy of the self associating copolymer (SAA14) at T_g and ΔH_M is the heat of mixing determined at T_g(blend).

As illustrated in Figs. 5 and 6, our calculations using the standard equilibrium constant and enthalpy of acid-acid hydrogen bonding self-association (K_2^{STD} = 1900 and $-h_B$ = 26.92 kJ/mol) for SAA14 previously determined, showed good agreement with the experimental values for a standard equilibrium constant and an enthalpy of acid-base hydrogen bonding inter-association (K_A^{STD} = 1100 and $-h_A$ = 31.40 kJ/mol) for SAA14/S4VP15 system and of (K_A^{STD} = 800 and $-h_A$ = 15.07 kJ/mol) for SAA14/SAD25 system.

These results showed negative enthalpy of mixing in the whole composition range and negligible contribution of the acidic constituent for SAA14/S4VP15.

An unusual behavior is however observed with SAA14/SAD25 system for which a reasonable agreement with the experimental values are obtained for both K_A^{STD} = 800 and $-h_A$ = 15.07 kJ/mol, smaller than those describing the self-association. A positive enthalpy of mixing is obtained in the whole composition range. This confirms that a negative enthalpy of mixing may not be necessary to obtain a miscible pair of polymers when entropy changes are associated with specific interactions [16].

According to this method, the positive variation in the plot of T_g-composition is mainly due to the large negative heat of mixing following the strong specific interactions occurring within the SAA14/S4VP15 blend. At the opposite, the negative variation in the plot of T_g-composition, for the SAA14/SAD25 system, seems to be the result of an endothermic heat of mixing as shown in Fig. 6. In this case, favourable non combinatorial entropic factors, originated from the disorientation of the self-associating component upon mixing, guarantee the miscibility of the system.

Table 3

T_gs of SAA14/S4VP15/SAD25 ternary polymer blend system.

SAA14/S4VP15/SAD25	T_g (exp) (°C)	T_g (lin) (°C)	T_g (Fox) (°C)	T_g (Kwei) (°C)
1/0/0	119	119	119	119
10/1/1	112*	116	116	116
3/0/1	110	114	113	108
3/1/0	119	116	115	120
4/1/1	104*	113	113	112
7/1/4	99*	111	110	106
7/4/1	108*	113	112	115
1/1/0	117	112	111	117
2/1/1	106*	110	109	109
1/0/1	99	109	107	101
5/2/5	96...109	108	107	104
5/5/2	104...121	110	109	111
1/1/1	107*	107	106	106
4/1/7	97	106	105	100
4/7/1	112*	109	108	112
1/0/3	98	103	102	97
1/3/0	113	108	108	112
1/1/2	103...114	105	104	102
1/2/1	98...126	106	106	107
1/4/1	112*	107	107	111
1/1/4	95	102	102	99
2/5/5	103...114	104	104	103
1/1/10	98	100	100	98
1/4/7	101...112	102	101	101
1/7/4	106...112	103	103	103
1/10/1	105...111	105	105	106
0/1/0	104	104	104	104
0/0/1	97	97	97	97

* Large transition.

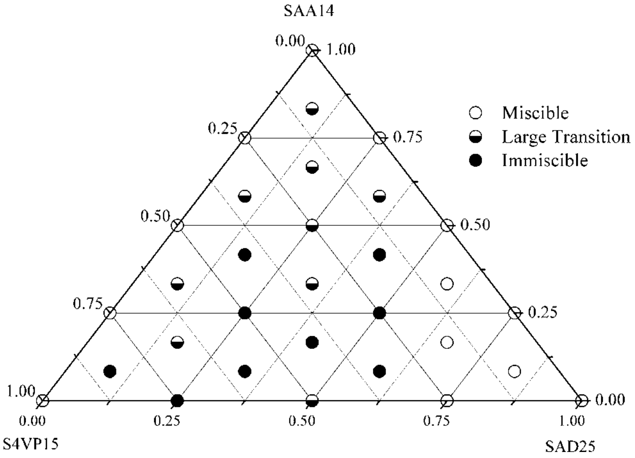

Fig. 10. Experimental phase diagram of SAA14/S4VP15/SAD25 ternary polymer blend.

S4VP15 and SAD25 do not develop any specific interactions of Hydrogen-bonding type and have close non-hydrogen-bonded solubility parameters that imply a weak $\Delta\chi$ effect.

Even though a single and narrow transition is observed with each composition of these blends, a DSC analysis of this binary system is rather difficult to assess the formation of a single phase since the difference between their glass transition temperatures is of 7 °C only.

3.2. Thermal analyses of SAA14/S4VP15/SAD25 ternary blend

Based on the results above and those reported in the literature [20], we undertook a study containing these three binary blends of similar polymer matrix in which SAA14 interacts with different strength with each of S4VP15 and SAD25, to investigate the phase behaviour of such ternary systems.

Fig. 7 shows selected second scan DSC thermograms of SAA14/S4VP15/SAD25 ternary blends with various compositions. Different miscibility behaviours are observed with these ternary polymer blends as a single or two T_gs are observed. The presence of more than one T_g observed in the thermogram is an evidence of phase separation, while the detection of one T_g is not sufficient to conclude the presence of a single homogeneous phase. Indeed, Fig. 8, displays some ternary blends such as SAA14/S4VP15/SAD25 1/2/1 and 1/1/2 that exhibited two transitions as confirmed from their first derivatives indicating their heterogeneity and others showing a single T_g with relatively narrow transitions such as 1/1/10 ternary blend.

Assuming that no hydrogen bonding interactions occurred between S4VP15 and SAD25 the modified Kwei equation below [21] was used to describe the ternary blend:

$$T_g(\text{blend}) = w_1 T_{g,1} + w_2 T_{g,2} + w_3 T_{g,3} + q_{12} w_1 w_2 + q_{13} w_1 w_3 \qquad (6)$$

The values of the experimental T_g obtained by DSC and those calculated from the equation above and the well-known Fox relation are summarized in Table 3. As illustrated in Fig. 9, the predicted values using the modified Kwei equation are in a fair agreement with those obtained experimentally.

Fig. 10 displays a triangular phase diagram of the ternary polymer blend based on the DSC analyses in which the solid and open circles stand for compositions that exhibited two and one T_g respectively. The presence of a significant heterogeneous region of the phase diagram is mainly due to the ΔK effect as already reported [18] since the $\Delta\chi$ effect is rather weak.

4. Conclusion

The miscibility and phase behaviour of binary SAA14/S4VP15, SAA14/SAD25 homoblends and SAA14/S4VP15/SAD25 ternary systems of different ratios investigated by DSC showed that SAA14 is miscible with both S4VP15 and SAD25 and interacts more strongly with S4VP15 than with SAD25 evidenced from different compositional variation of glass transition temperatures (T_g) as positive and negative deviations from linear average line were respectively observed with the SAA14/S4VP15 and SAA14/SAD25 blends.

These T_g-composition behaviours were analyzed by several conventional theoretical approaches including that of Coleman et al. and the one very recently proposed by Brostow et al.

The one parameter Gordon–Taylor equation or the two parameters Kwei equation describe very well the SAA14/S4VP15 compositional behaviour of the T_g. However, the recent three parameters Brostow equation was needed to reproduce experimental T_g-composition for the SAA14/SAD25 system.

The theoretical fitting parameter free method developed by Coleman et al., applied to predict the composition dependence of the T_g of both SAA14/S4VP15 and SAA14/SAD25 systems, showed reasonable agreement with the experimental values.

Due to the unbalanced interactions that occurred between the different constituents, an immiscibility region is observed within the experimental phase diagram of the SAA14/S4VP15/SAD25 ternary polymer blend as analyzed by DSC.

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