

## Miscibility and LCST Behavior of Polyisoprene/ Poly(*cis*-butadiene-*co*-1,2-vinylbutadiene) Blends

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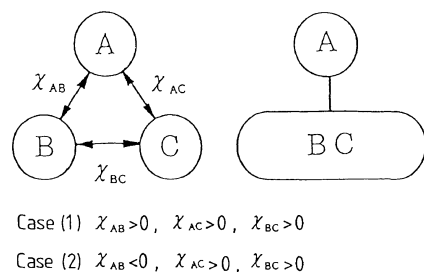
**ABSTRACT:** The miscibility of rubber blends, such as poly(*cis*-butadiene-*co*-1,2-vinylbutadiene) (V-BR) and polyisoprene (IR), was studied with differential scanning calorimetry (DSC), torsion braid analysis (TBA) and transmission electron microscopy. The V-BR with high vinyl content above 32.3 wt% was miscible with IR, while the V-BR with lower vinyl content less than 24.3 wt% was immiscible. In regard to V-BR (32.3)/IR blends the lower critical-solution-temperature (LCST) type phase diagram was shown by means of the glass transition ( $T_g$ ) behavior of annealed blends. The miscible and immiscible phase boundary would be sharp against the random copolymer content (at around 30 wt% vinyl content in V-BR). The  $T_g$  behavior of these miscible blends were in good agreement with Gordon-Taylor equation. In addition to DSC and TBA measurements the transmission electron micrographs were obtained to confirm the blend morphology in the ultra-thin sections stained with osmium tetroxide.

**KEY WORDS** Miscibility / Random Copolymer / Polyisoprene / Vinyl Polybutadiene / Annealing Study / LCST Phase Behavior / Thermal Reversibility / Torsional Braid Analysis / DSC Thermograms / Transmission Electron Microscopy /

The phase behavior of polymer-polymer mixtures has been investigated and summarized in several literatures.<sup>1-3</sup> Although some theories<sup>4-7</sup> were developed, the miscibility of polymer-polymer blends has been empirically investigated<sup>8-11</sup> because of the difficulty of theoretical approaches. Akiyama<sup>12,13</sup> has pointed out the following five methods of how to achieve polymer compatibility: (1) effect of favorable interactions between polar polymer pairs, (2) contribution of random copolymerization to polymer miscibility, (3) effect of high pressure onto miscible blend, (4) utilization of compatibilizer (block or graft copolymer), (5)

formation of interpenetrating polymer network (IPN).

Among these methods, the contribution of random copolymerization (2) is remarkable.<sup>9,14</sup> For a blend of homopolymer (A) with random copolymer (BC) composed of monomeric species B and C, the miscible combinations can be divided empirically into the following two cases as shown in Figure 1: (1) All the interaction parameter,  $\chi_{AB}$ ,  $\chi_{AC}$  and  $\chi_{BC}$ , are positive, in which case all these pairs of the homopolymers are immiscible due to the unfavorable enthalpy of mixing; and (2)  $\chi_{AC}$  is negative, but  $\chi_{AB}$  and  $\chi_{BC}$  are positive, in which



**Figure 1.** Schematic representation of miscible binary blends, homopolymer/random copolymer.

case the pair of A and C is miscible but others are immiscible. In the case of the blend of homopolymer (A) with binary random copolymer (BC), the miscibility window<sup>15,16</sup> is obtained as a function of the copolymer composition for the blend delineating the locus of LCST's; for example, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with poly(*o*-chlorostyrene-*co*-*p*-chlorostyrene) (poly(*o*CIS-*co*-*p*CIS)),<sup>15</sup> PPO with poly(*o*-fluorostyrene-*co*-*p*-fluorostyrene) (poly(*o*FS-*co*-*p*FS))<sup>16</sup> and poly(methyl methacrylate) (PMMA) with poly(styrene-*co*-acrylonitrile) (SAN)<sup>17</sup> blends, and the "miscibility valley"<sup>13</sup> is newly predicted, delineating the locus of the UCST's; for example, poly(carbonate) (PC) with poly(styrene-*co*-methacrylic acid) (poly(S-*co*-MAA))<sup>18,19</sup> blend. On the other hand, in the second case, choosing the blend of A and BC, the miscibility door is predicted<sup>14</sup> on the temperature-copolymer composition plot. The V-BR/IR<sup>20</sup> blend could be the second case, where the blend of 1,2-polybutadiene with polyisoprene is presumed miscible and both of 1,4-polybutadiene with polyisoprene and 1,2-polybutadiene with 1,4-polybutadiene are immiscible. Other examples in the second case are PPO with poly(styrene-*co*-*p*-chlorostyrene) (poly(S-*co*-*p*CIS)),<sup>21</sup> PMMA with poly(vinylidene fluoride-*co*-tetrafluoroethylene) (poly(VDF-*co*-TFE)),<sup>22</sup> poly(vinyl acetate) (PVAc) with poly(vinylidene fluoride-*co*-hexafluoroacetone) (poly(VDF-*co*-HFA))<sup>23,34</sup> and PC with poly(vinyl phenol-*co*-styrene) (poly(pVPh-*co*-

S)).<sup>24</sup>

Zlatkevich and Nikolskii<sup>25</sup> said in their report that the V-BR(30)/IR blend exhibited the same miscible single  $T_g$  behavior as V-BR(30)/BR, V-BR(50)/BR, V-BR(60)/BR and V-BR(30)/NR blends without annealing. The figures in parentheses represent the vinyl contents in wt% of V-BR. They obtained an empirical equation for the composition dependency of  $T_g$  of blends, which is different from the Gordon-Taylor equation and Fox equation.

Nishi and co-workers<sup>26</sup> investigated various V-BR/V-BR blend miscibilities with the phase contrast microscope, DSC and pulsed NMR. These blends were classified into miscible and immiscible, but the phase diagrams were not obtained.

Moreover, recently, high vinyl polybutadiene (V-BR)/polyisoprene blends<sup>27</sup> are also reported to exhibit an excellent balance of rebound resilience and wet skid resistance. At the same time, on the base of DSC measurement, the V-BR(71)/IR blend is shown to be miscible and V-BR(11)/IR blend is immiscible at 5/5 blend ratio.

In the present paper, the miscibility of V-BR/IR is studied with respect to the copolymer composition in V-BR.  $T_g$  of annealed polymer blends are also investigated with DSC. In order to obtain the phase diagram,<sup>20</sup>  $T_g$  of the blend is measured after annealing at defined temperatures between  $-25$  and  $200^\circ\text{C}$  for 2 hours. At the same time, the miscible-immiscible boundary is determined as a function of random copolymer composition at the limited blend ratio.

## EXPERIMENTAL

Polybutadiene with various vinyl contents were prepared by polymerizing 1,3-butadiene in hexane or benzene with a *n*-butyllithium catalyst in combination with diglyme(diethylene glycoldimethyl ether) at  $40^\circ\text{C}$ . The molecular characteristics are shown in Table I.

**Table I.**  $T_g$  and molecular weight of the samples

Samples	$M_w$	$M_w/M_n$	$T_g/^\circ\text{C}$
IR	730000	1.84	-66
V-BR 71	484000	3.62	-35
V-BR 60.0	224000	1.04	-48
V-BR 54.3	267000	1.06	-55
V-BR 47.4	214000	1.03	-62
V-BR 32.3	214000	1.03	-73
V-BR 24.3	222000	1.04	-79
V-BR 11	219000	2.35	-96

The blend samples were prepared by precipitation from 5% toluene solutions in ethanol. The precipitated samples were dried under vacuum at 40°C for a week. When the samples were prepared through casting of solutions, all these as-cast blend films were transparent even after annealing at high temperatures such as 200°C for 2 h.

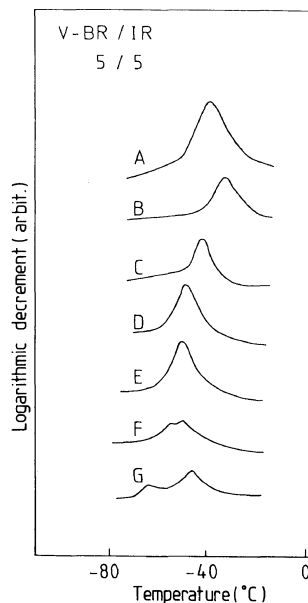
$T_g$  of blends was measured using a Du-Pont 990 DSC at a rate of 10°C min.<sup>-1</sup>  $T_g$  of the blends was defined as the point intersection between the base line and the tangent line at the inflection point of DSC thermograms.

Dynamic mechanical measurements of the blend samples were carried out using a hand-made torsion braid analyzer (TBA)<sup>28,29</sup>: the frequency was 2–3 Hz and the heating rate was about 1°C min.<sup>-1</sup>

Transmission electron micrographs were obtained on JEM 1200 EX (JEOL) electron microscope. The ultra thin sections were obtained from freeze-dried samples using LKB CRYO NOVA (JEOL). The samples were stained by osmium tetroxide for an hour.

## RESULTS AND DISCUSSION

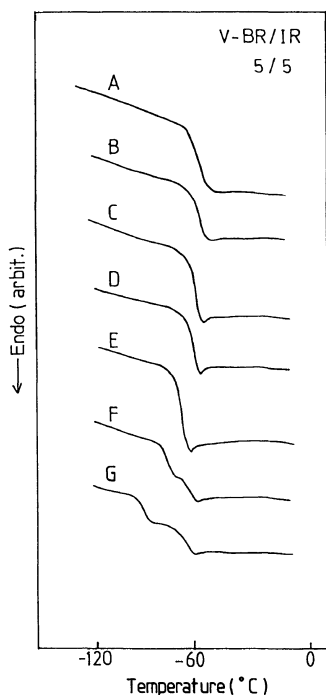
The dynamic mechanical properties of the V-BR/IR blends, 5/5 by weight, with various vinyl contents are shown in Figure 2. V-BRs with higher vinyl content from 47.4 to 71 wt% are miscible with IR because they have a single



**Figure 2.** TBA thermograms of V-BR/IR(5/5) blends with various vinyl contents. The thermograms represent vinyl contents of (A) 71, (b) 60, (C) 54.3, (D) 47.4, (E) 32.3, (F) 24.3, and (G) 11 wt%.

peak, while V-BRs with lower vinyl content from 11 to 24.3 wt% are immiscible because they have double peaks. Thus the miscible-immiscible boundary seems to be around 30 wt% vinyl content. In Figure 3, the same results on the miscibility for V-BR/IR blends are shown through DSC measurements. The miscible blend  $T_g$  shifts smoothly depending on the vinyl content. The blends with vinyl content less than 24.3 wt%, have two  $T_g$ 's, *i.e.*, one is for IR and the other for V-BR.

When the blend composition is varied, the single  $T_g$  of the miscible blend systematically shifts between  $T_g$ 's for the pure V-BR and IR. The variation of  $T_g$  for the V-BR(71)/IR blends with annealing between -25 and 200°C for 2 h is shown in Figure 4. Three equations are available for the  $T_g$  of these miscible blends. First, it is the conventional Gordon-Taylor equation<sup>30</sup> giving eq 1 to a random copolymer composed of two monomers.



**Figure 3.** DSC thermograms of V-BR/IR(5/5) blends with various vinyl contents. The thermograms represent vinyl contents of (A) 71, (B) 60, (C) 54.3, (D) 47.4, (E) 32.3, (F) 24.3, and (G) 11 wt%.

$$T_g = \frac{T_{g_1} + (KT_{g_2} - T_{g_1})W_2}{1 + (K-1)W_2} \quad (1)$$

where  $T_{g_1}$  and  $T_{g_2}$  is the  $T_g$  of the pure V-BR and IR, respectively,  $W_2$  is the weight fraction of V-BR and  $K$  is the ratio of the thermal expansion coefficient of the amorphous states and of the glassy states.

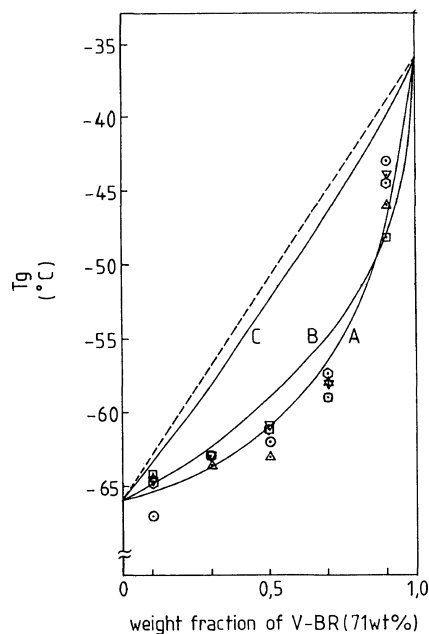
Second is Fox equation<sup>31</sup>:

$$\frac{1}{T_g} = \frac{(1-W_2)}{T_{g_1}} + \frac{W_2}{T_{g_2}} \quad (2)$$

Third is a simple empirical equation for the  $T_g$  of a binary blend of dissimilar elastomers, introduced by Zlatkevich and co-workers.<sup>25</sup>

$$T_g = T_{g_2} - (T_{g_2} - T_{g_1}) \cdot W_1^C \quad (3)$$

where  $W_1$  is the weight fraction of the elastomer with the lower glass transition temperature and  $C$  is a constant for a given polymer-polymer mixture system.

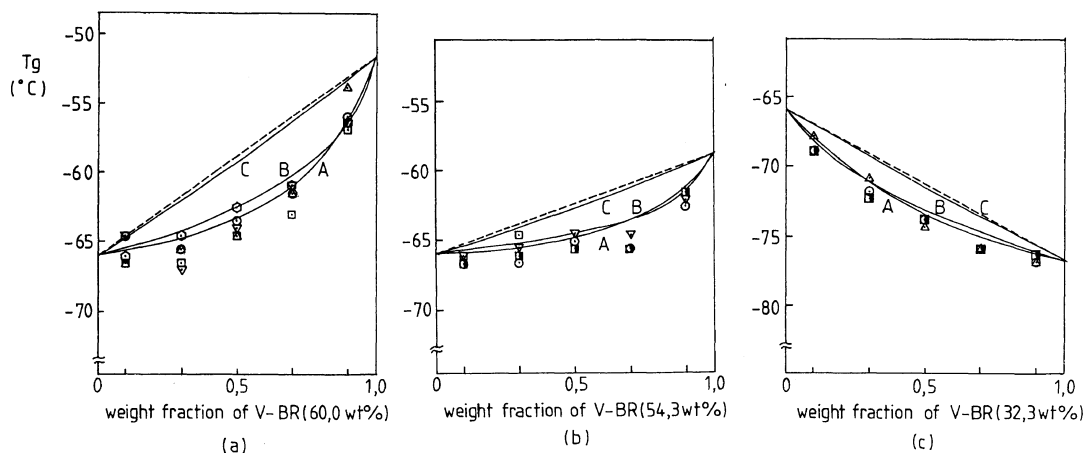


**Figure 4.** Glass transition temperature ( $T_g$ ) of miscible V-BR(71)/IR blend at various annealing temperatures: ( $\Delta$ ),  $-25^\circ\text{C}$ , ( $\circ$ ),  $25^\circ\text{C}$ , ( $\square$ ),  $100^\circ\text{C}$ , ( $\nabla$ ),  $150^\circ\text{C}$ , and ( $\diamond$ ),  $200^\circ\text{C}$  for 2 h; (A) Gordon-Taylor curve ( $K=0.21$ ); (B) Zlatkevich curve; (C) Fox curve.

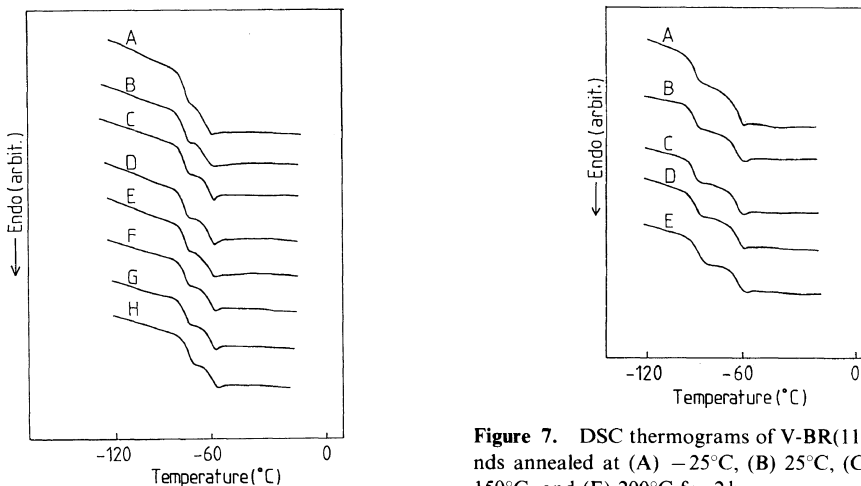
In Figure 4 the solid curve A corresponds to the Gordon-Taylor equation, B to the Zlatkevich equation, C to the Fox equation, and the dashed line is the straight line between  $T_g$ 's of constituent elastomers. It was informed by Zlatkevich that  $T_g$  of the miscible elastomers, e.g., V-BR/IR, was well explained with their equation.<sup>25</sup> In this study,  $T_g$  of blend annealed can be well explained by Gordon-Taylor equation rather than Zlatkevich's. The same results are also obtained in V-BR(60)/IR, V-BR(54.3)/IR, and V-BR(32.3)/IR as shown in Figure 5 (a), (b), and (c), respectively.

The miscible blends are obviously stable at any annealing temperatures between  $-25$  and  $200^\circ\text{C}$ , except for V-BR(32.3)/IR, because no double  $T_g$  appeared through these thermal treatments.

The DSC thermograms of V-BR(24.3)/IR 5/5 blends annealed at various temperatures between  $-25$  and  $200^\circ\text{C}$  for 2 h are shown



**Figure 5.** Glass transition temperature ( $T_g$ ) of miscible blends, (a) V-BR(60)/IR ( $K=0.22$ ), (b) V-BR(54.3)/IR ( $K=0.22$ ), and (c) V-BR(32.3)/IR ( $K=2.5$ ), at various annealing temperatures: ( $\Delta$ ),  $-25^\circ\text{C}$ ; ( $\circ$ ),  $25^\circ\text{C}$ ; ( $\blacksquare$ ),  $50^\circ\text{C}$ ; ( $\square$ ),  $100^\circ\text{C}$ ; ( $\nabla$ ),  $150^\circ\text{C}$ ; ( $\odot$ ),  $200^\circ\text{C}$ .



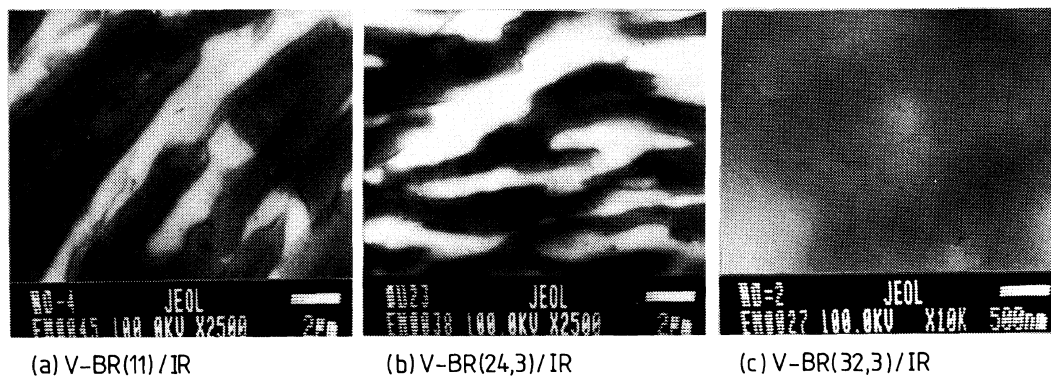
**Figure 6.** DSC thermograms of V-BR(24.3)/IR(5/5) blends annealed at (A)  $-25^\circ\text{C}$ , (B)  $25^\circ\text{C}$ , (C)  $50^\circ\text{C}$ , (D)  $75^\circ\text{C}$ , (E)  $100^\circ\text{C}$ , (F)  $125^\circ\text{C}$ , (G)  $150^\circ\text{C}$ , and (H)  $200^\circ\text{C}$  for 2 h.

**Figure 7.** DSC thermograms of V-BR(11)/IR(5/5) blends annealed at (A)  $-25^\circ\text{C}$ , (B)  $25^\circ\text{C}$ , (C)  $100^\circ\text{C}$ , (D)  $150^\circ\text{C}$ , and (E)  $200^\circ\text{C}$  for 2 h.

in Figure 6. The V-BR(24.3)/IR blend is immiscible because of the double  $T_g$ . In order to find the phase diagram, the same tests were carried out at various annealing temperatures, from  $-25$  to  $200^\circ\text{C}$ , and for various time of length, from 2 h to 2 days. At lower annealing temperatures, the thermogram of double  $T_g$  is close to that of single  $T_g$ . However, at higher annealing temperatures the

thermogram of double  $T_g$  can be clearly seen, *i.e.*, at  $T_g$  of each component polymer. Thus the phase separation grows as the temperature rises. This blend has no miscible region at any temperatures between  $-25$  and  $200^\circ\text{C}$ .

As shown in Figure 7, the V-BR(11)/IR blend is also immiscible. However the  $T_g$  doesn't change with annealing at various temperatures. Therefore, comparing with the V-BR(24.3)/IR blend, it may be considered that the V-BR(11)/IR blend satisfies the condition in which the phase separated structure is fixed



**Figure 8.** TEM photographs of V-BR/IR blends containing (a) 11, (b), 24.3, and (c) 32.3 wt% 1,2-butadiene.

and stable against annealing.

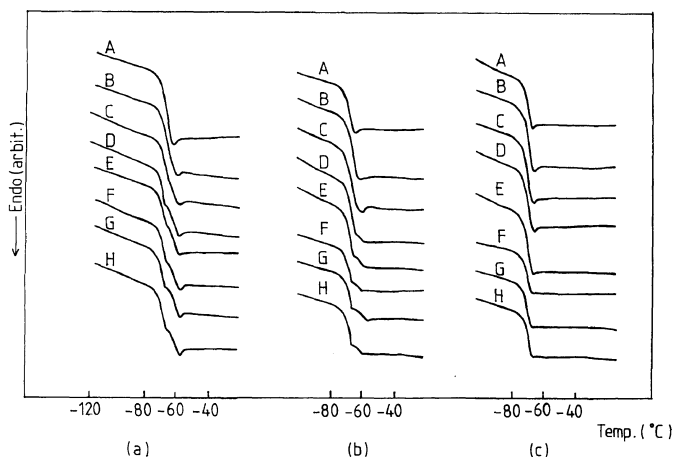
The transmission electron micrographs of V-BR/IR blends, 5/5 by weight, with lower vinyl contents, 11, 24.3 and 32.3 wt%, are shown in Figure 8. The double bonds of V-BR and IR can be stained by  $\text{OsO}_4$ . In stained V-BR(11)/IR blends the phase contrast microscopic observation is indicated that the gloomy domain increases as V-BR increases. We found that time limit to stain the blends (just one hour) is necessary to distinguish V-BR from IR. The bright domain is IR and the gloomy domain is V-BR. The electron micrographs (a) and (b) in Figure 8 show the phase separated structures for the V-BR(11)/IR and the V-BR(24.3)/IR, respectively, which correspond to the results of the double  $T_g$  by TBA and DSC. The phase separated structure (b) of the V-BR (24.3)/IR has a morphology like that of well-known spinodal decomposition with the unique periodicity and the high phase connectivity. The (a) of V-BR(11)/IR shows larger domain sizes than (b) and somewhat discontinuity. On the other hand, in the V-BR(32.3)/IR the domains in the blends becomes less than  $100 \text{ \AA}$  in size (in photograph (c)). The V-BR(11) with the least vinyl content is the most immiscible blend. This blend has a larger domain size than V-BR(24.3)/IR. This may lead us to conclude that the miscibility of V-BR/IR blend decreases with decreasing vi-

nyl content in V-BR.

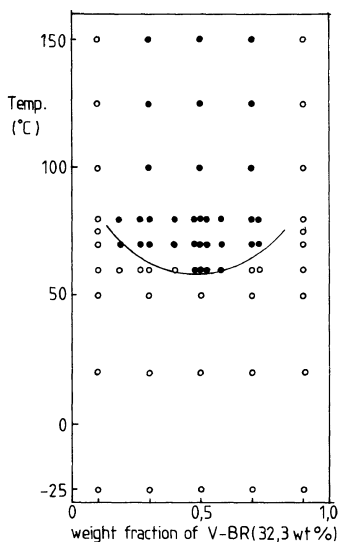
#### LCST Behavior

The phase diagram was observed through a series of annealing experiments. The V-BR(32.3)/IR blends are miscible at annealing temperatures between  $-25$  and  $50^\circ\text{C}$  as mentioned above. But the double  $T_g$  is observed at higher annealing temperatures. The typical DSC thermograms of blends with 5/5, 7/3, and 9/1 by weight are shown as a function of annealing temperature in Figure 9 (a), (b), and (c), respectively. As is clearly seen, the 5/5 and 3/7 blends exhibit double  $T_g$  with rising the temperature, while in the 9/1 blend double  $T_g$  can not be detected. For the experimental data in LCST phase diagram, annealing time was two-hours, and the temperature of phase transition was defined as the annealed temperature where  $T_g$  changes from the single one to the double one in DSC thermograms. In this way is evaluated the LCST phase diagram in Figure 10: double  $T_g$  (immiscible) above the solid line, and single  $T_g$  (miscible) below the line. The phase boundary temperature smoothly changes along a concave curve with the blend composition.

It was also found that on this LCST phase diagram the change of  $T_g$  from the double one to the single one took place reversibly.<sup>32</sup> As shown in Figure 11, the V-BR (32.3)/IR blend

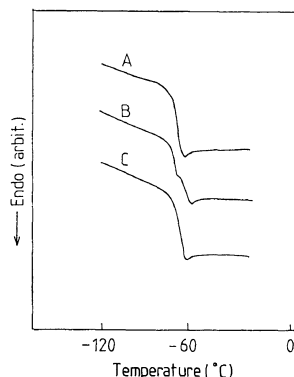


**Figure 9.** DSC thermogram changes from single  $T_g$  to double  $T_g$  by elevating temperatures of V-BR(32.3)/IR blends containing (a) 50, (b) 70, and (c) 90 wt% V-BR; (A), 25°C; (B), 50°C; (C), 60°C; (D), 70°C; (E), 80°C; (F), 100°C; (G), 125°C; (H), 150°C.



**Figure 10.** LCST phase diagram of V-BR(32.3)/IR blends, obtained by  $T_g$  measurements: ●, double  $T_g$ ; ○, single  $T_g$ .

annealed at 100°C for 2 h which has double  $T_g$  becomes to show a single  $T_g$  when annealed at 25°C for an hour. More detailed studies showed that the miscible state can be achieved at 25°C for about 10 min after annealing at 100°C for 3 h, and the reversibility has been confirmed even after annealing at 100°C for a day in vacuum. Thus the



**Figure 11.** Reversible phase behavior revealed in DSC thermograms, (A) as-cast original sample, (B) annealed at 100°C for 2 h, and (C) left at 25°C for a day after annealing.

LCST behavior is confirmed in the V-BR(32.3)/IR, and the reversible  $T_g$  change from the double one to the single one are also observed. The same reversible miscible-immiscible transition takes place in the blends of poly(vinyl nitrate) (PVN) with poly(methyl acrylate),<sup>32,33</sup> poly(VDF-co-HFA) with poly(ethylene-co-vinylacetate) (EVAc)<sup>34</sup> and poly(VDF-co-HFA) with PMMA<sup>23</sup> which have been already reported in the previous papers.

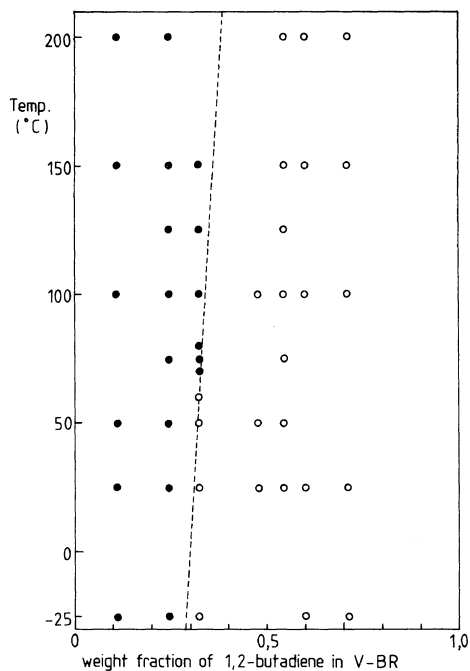
## CONCLUSION

The butadiene random copolymer (V-BR) with vinyl contents above 32.3 wt% is miscible with IR. The composition dependence of  $T_g$  follows the Gordon-Taylor equation. Thus the elastomer blends of V-BR(71)/IR, V-BR(60)/IR, and V-BR(54.3)/IR are found to be miscible. If the vinyl content in V-BR was decreased, the miscibility decreases and below 24.3 wt% vinyl contents the phase separation occurs. In this study, in regard to V-BR(32.3)/IR blend the LCST phase diagram is obtained by  $T_g$  measurements, and the reversible phase transitions are confirmed. The phase behavior of V-BR/IR blends as a function of the random copolymer compositions (vinyl contents) in Figure 12 may be the same type as already reported "miscibility door",<sup>14</sup> and more detailed investigation are being now undertaken.

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**Figure 12.** Miscibility phenomena against 1,2-butadiene compositions in random copolymer V-BR of V-BR/IR blends(5/5). ●, double  $T_g$ ; ○, single  $T_g$ .

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