

## PMMA/PVME

(2001 6 22, 2002 1 11)

### Thermodynamic Characteristics of PMMA/PVME Blends Containing Compatibilizer and Their Gas Transport Properties

H. W. Choi, Y. J. Moon, B. J. Jung, and C. K. Kim<sup>†</sup>

Department of Chemical Engineering, Chung-Ang University,  
221 Heuksuk-dong, Dongjak-Gu, Seoul 156-756, Korea

<sup>†</sup>e-mail: ckkim@cau.ac.kr

(Received June 22, 2001; accepted January 11, 2002)

poly(styrene-*b*-methylmethacrylate) [P(S-*b*-MMA)]  
 polymethylmethacrylate (PMMA) polyvinylmethylether (PVME)  
 poly(styrene-*co*-methylmethacrylate) (SMMA)  
 PVME  
 SMMA/PVME LCST  
 PMMA/PVME  
 P(S-*b*-MMA) 가 5 phr 가  
 가 5 phr 가

**ABSTRACT :** Thermodynamics and gas transport properties of polymethylmethacrylate (PMMA) blends with polyvinylmethylether (PVME) containing various amount of poly(styrene-*b*-methylmethacrylate) copolymer (P(S-*b*-MMA)) as a compatibilizer were studied. To extract interaction energies of binary pairs involved in the blends from the phase separation temperatures using an equation-of-state theory, PVME blends with methylmethacrylate copolymers containing various amount of styrene (SMMA) were prepared. PVME formed miscible blends with methylmethacrylate copolymers containing more than 70 wt% styrene and these miscible blends showed a LCST-type phase separation behavior. Based on the interaction information obtained here, P(S-*b*-MMA) copolymer was added to the PMMA/PVME blends to enhance their compatibility. The average diameter of the dispersed rubber particles was gradually decreased for the blends of containing P(S-*b*-MMA) from 0 to 5 phr and then leveled off at a fixed size. At a fixed blend composition, the gas permeation was also increased as the P(S-*b*-MMA) content increased from 0 to 5 phr and then leveled off when the P(S-*b*-MMA) content was higher than 5 phr.

**Keywords :** PMMA/PVME blends, interaction energy, domain size, compatibilization, gas permeation.

가

<sup>11</sup>

PMMA

가

PVME

, PMMA/PVME

가

P(S-b-MMA)

<sup>1,2</sup>

가

PMMA

가

PVME

, PVME

PVME

PMMA

P(S-b-MMA)

PVME

가

가

/

/

가

<sup>3-10</sup>

가

가

가

가

(percolation)

가

가

Table 1

PMMA LG

HF2770

(reactive 82000

2.00

compatibilizer) 96000 PVME Aldrich

SMMA

가

가

가

가가

가

2,2' - azo - bis - isobutyrylnitrile (AIBN) 0.5 wt%,

20 wt%

PMMA/PVME

Table 1. Polymers Used in This Study

abbreviation	polymer	$\overline{M}_w$	styrene content <sup>f</sup> (wt%)	source
PVME	Polymethylmethacrylate	82000 (2.00)	-	LG Chemical LG HF2770
PVME	polyvinylmethylether	96000 (2.12)	-	Aldrich
P(S-MMA)95	poly(styrene-co-methylmethacrylate)	150000 (1.92)	95.2	synthesized
P(S-MMA)85	"	134000 (2.32)	84.5	"
P(S-MMA)80	"	178500 (2.55)	79.6	"
P(S-MMA)75	"	146000 (2.41)	74.9	"
P(S-MMA)70	"	137000 (2.81)	69.1	"
P(S-MMA)65	"	146500 (2.34)	64.2	"
P(S-MMA)50	"	176000 (2.55)	5.6	"
P(S-b-MMA)	poly(styrene-b-methylmethacrylate)	192000 (1.05)	18	Aldrich

\* Styrene content in copolymer was determined from the element analysis.

80 ,  
30  
10 wt%  
GPC (JASCO Model 2350)  
가  
가 N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> 가 ( )  
99.99% ,  
(RGF 12-400, Labclear Inc.)  
5 wt%  
60  
, 60  
PMMA PVME 2  
wt%

가  
60  
가  
60  
PVME가  
50 μm  
PS/PVME, SMMA/PVME  
LCST hot stage  
[Linkam, THMS 600] central processor  
[Linkam, TMS92] image analyzer [Bummi universe]  
hot stage , central processor  
2  
1 morphology  
image analyzer  
12,13  
image  
analyzer 10  
downstream  
가  
constant volume method  
(upstream)  
(downstream)  
가  
downstream  
time-lag  
Q (1)  
$$\Delta Q = \frac{\Delta pVT}{760(T_o + T)} \quad (1)$$
  
, p downstream , T<sub>o</sub>  
273.15K , T  
( ) (2)  
$$P = \frac{\Delta QL}{\Delta t \Delta p_o} \quad (2)$$

STP, Q, L, upstream, P(S-MMA)/PVME, SMMA, Table 1, PVME, 70 wt%, 70 wt%, PVME, PVME/SMMA, LCST, PVME/SMMA, Figure 1, SMMA, PVME, 70-80 wt%, Figure 2, MMA, PVME/SMMA, PVME/SMMA, MMA, 가, 가, 가, MMA, 25 wt%, 가, MMA, 30 wt%, PVME/SMMA

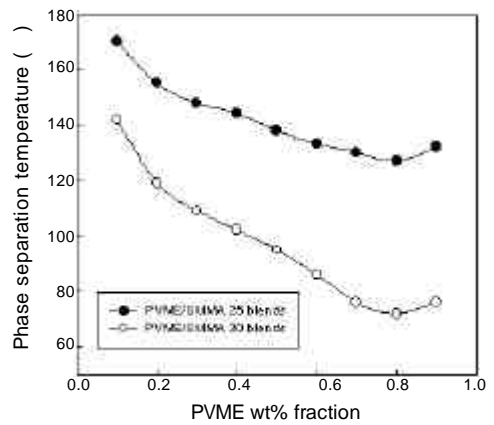
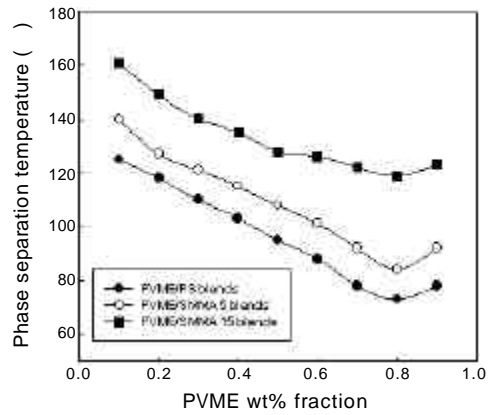


Figure 1. Phase separation temperatures of PVME blends with styrenic copolymers containing various amount of MMA.

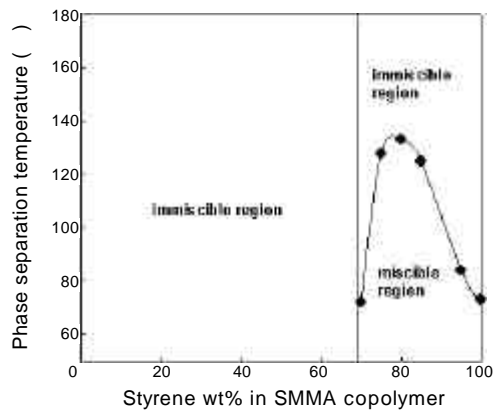


Figure 2. Miscibility windows of PVME/SMMA=8/2 blends.

interaction model, fluid theory model, PVME/SMMA, binary, lattice - binary interaction, P<sup>\*</sup><sub>VME-S</sub>, P<sup>\*</sup><sub>VME-MMA</sub>, P<sup>\*</sup><sub>S-MMA</sub>

PMMA/PVME

15  
 $P_{VME-S}^* = -0.28 \text{ cal/cm}^3$ ,  $P_{VME-MMA}^* = 1.81 \text{ cal/cm}^3$   
 $P_{S-MMA}^* = 0.21 \text{ cal/cm}^3$   
 VME  $P_{VME-S}^* = -0.28 \text{ cal/cm}^3$   
 PVME 가

$P_{VME-MMA}^* = 1.81 \text{ cal/cm}^3$   
 $P_{S-MMA}^* = 0.21 \text{ cal/cm}^3$  PVME/ PMMA  
 PS/PMMA 가  
 PVME/PMMA  
 가 가

가

P(S-b-MMA)가 PMMA/PVME

PMMA/PVME  
 PVME 20 wt%

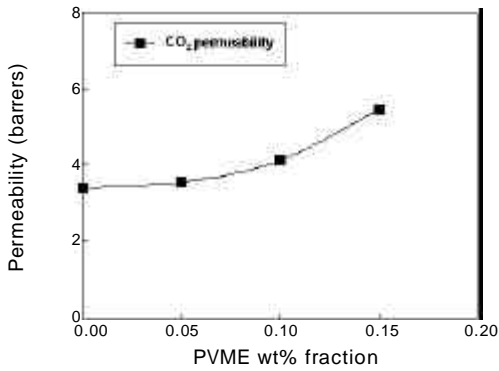
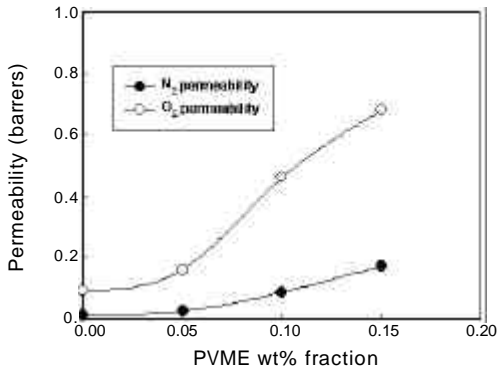
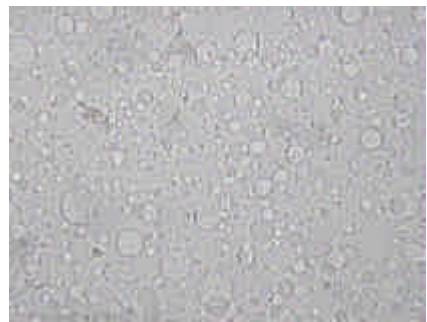
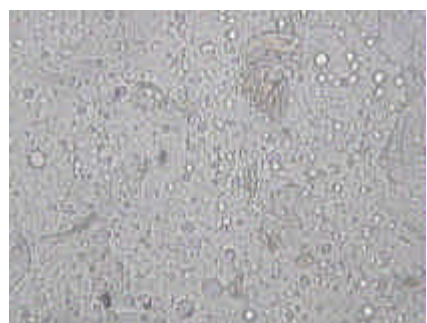


Figure 3. Changes in gas permeability of PVME/PMMA blends with PVME content.

가  
 PVME 20 wt%  
 Figure 3 PMMA/PVME  
 가 가  
 PVME 10 wt%



(a)

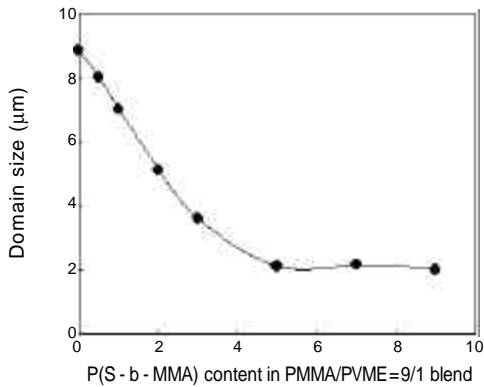


(b)

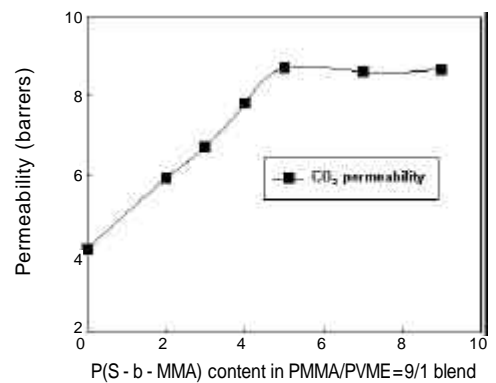
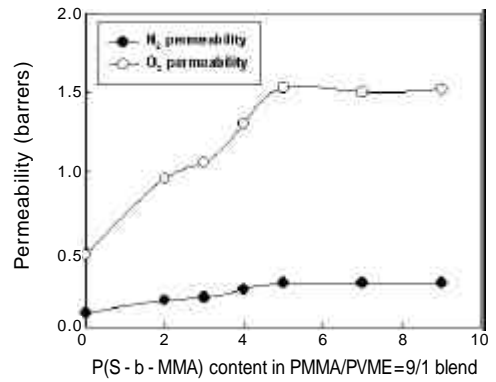


(c)

Figure 4. Morphology of PMMA/PVME=9/1 blends controlled by P(S-b-MMA) copolymer. (a) without block copolymer, (b) with 2 phr block copolymer, and (c) with 5 phr block copolymer.



**Figure 5.** The effects of compatibilizer content on the average size of dispersed particles in the PMMA/PVME=9/1 blends.



**Figure 6.** Gas permeability of PMMA/PVME=9/1 blends with P(S-b-MMA) content.

가  
4 image analyzer

가  
8.8 μm P(S-b-MMA)  
가  
Figure 5

가  
가 5 phr

가  
, ,  
, , /  
PVME  
P(S-b-MMA) 가  
Figure 6

가  
가  
(0-5 phr)  
가 5 phr 가  
가 /  
1 bar 0.5 bar 3 bar  
가  
method time lag

가  
time lag method  
Figure 7

5 phr 가 가  
가

가

PMMA/PVME

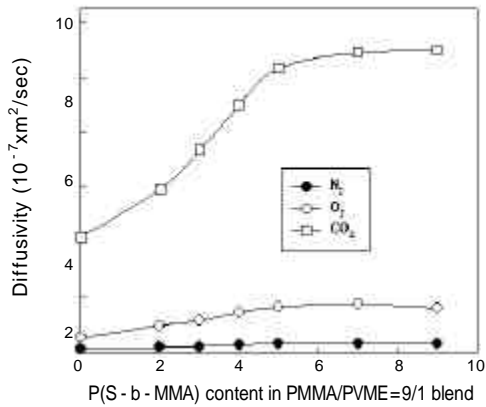


Figure 7. Changes in the diffusivity of PMMA/PVME=9/1 blends with P(S-b-MMA) content.

P(S-b-MMA)  
 PMMA/PVME

PMMA

PVME

PMMA PVME

PVME

8.8 μm

LCST UCST  
 가 . PMMA/ PVME

SMMA PVME

70 wt% SMMA/PVME

LCST

SMMA/PVME

$P^*_{VME-S} = -0.28 \text{ cal/cm}^3$ ,  $P^*_{VME-MMA} = 1.81 \text{ cal/cm}^3$ ,  $P^*_{S-MMA} = 0.21 \text{ cal/cm}^3$

-VME PS/PVME

VME-MMA S-MMA  
 PVME/ PMMA PS/

PMMA 가 ,  
 PVME/PMMA 가

가

가 가 5 phr

가

가 5 phr

가 ,  
 가

가 : 2000  
 ( )  
 ARC (Applied Rheology Center)

1. L. M. Robeson, *J. Memb. Sci.*, 62, 165 (1991).  
 2. W. J. Koros and D.R. Paul, *J. Polym. Sci.: Part B*, 14, 675 (1976).  
 3. M. Mulder, "Basic Principles of Membrane Technology", Kluwer Academic Pub., Dordrecht,

- Netherlands, 1996.
4. J. Csernica, R. F. Baddour, and R. E. Cohen, *Macromolecules*, 22, 1492 (1989).
  5. J. Csernica, R. F. Baddour, and R. E. Cohen, *Macromolecules*, 23, 1429 (1990).
  6. Y. J. Shur and B. G. Ranby, *J. Appl. Polym. Sci.*, 19, 1337 (1975).
  7. C. H. M. Jacques and H. B. Hopfenberg, *Polym. Eng. Sci.*, 14, 499 (1974).
  8. J. Sax and J. M. Ottino, *Polym. Eng. Sci.*, 23, 165 (1983).
  9. J. M. Ottino and N. Shah, *Polym. Eng. Sci.*, 24, 153 (1984).
  10. J. Sax and J. M. Ottino, *Polymer*, 26, 1073 (1985).
  11. R. P. Wool, "Polymer Interfaces, Structure and Strength", p. 336, Hanser Publishers, Cincinnati, 1989.
  12. C. K. Kim and D. R. Paul, *Polymer*, 33, 4929 (1992).
  13. J. H. Kim, D. S. Park, and C. Kim, *J. Polym. Sci.: Part B*, 38, 2666 (2000).
  14. D. R. Paul and J. W. Barlow, *Polymer*, 25, 487 (1984).
  15. P. A. Rodgers, *J. Appl. Polym. Sci.*, 48, 1061 (1993).
  16. I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.*, 80, 2352 (1976).
  17. I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.*, 80, 2568 (1976).
  18. I. C. Sanchez and R. H. Lacombe, *Macromolecules*, 11, 1145 (1978).
  19. I. C. Sanchez and A. C. Balazs, *Macromolecules*, 22, 2325 (1989).