Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Surface Structure of Polymethacrylate/SAN Blend Thin Films: Preliminary Contact Angle Studies

Guehyun Kim [a], Won-Ki Lee [b], Wonho Kim [c], Jin-Kook Lee [a] & Chang-Sik Ha [a]

[a] Department of Polymer Science and Engineering, Pusan National University, Pusan, 609-735, Korea

[b] Technical Research Laboratories, POSCO, Pohang, 790-785, Korea

[c] Department of Chemical Engineering, Pusan National University, Pusan, 609-735, Korea

Version of record first published: 29 Oct 2010

To cite this article: Guehyun Kim, Won-Ki Lee, Wonho Kim, Jin-Kook Lee & Chang-Sik Ha (2002): Surface Structure of Polymethacrylate/SAN Blend Thin Films: Preliminary Contact Angle Studies, Molecular Crystals and Liquid Crystals, 377:1, 341-344

To link to this article: http://dx.doi.org/10.1080/713738513

Mol. Cryst. Liq. Cryst., Vol. 377, pp. 341-344

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290089239

Surface Structure of Polymethacrylate/SAN Blend Thin Films: Preliminary Contact Angle Studies

GUEHYUN KIM[a], WON-KI LEE[b], WONHO KIM[c], JIN-KOOK LEE[a] and CHANG-SIK HA[a,*]

[a]*Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea,*
[b]*Technical Research Laboratories, POSCO, Pohang 790-785, Korea and*
[c]*Department of Chemical Engineering, Pusan National University, Pusan 609-735, Korea*

The purpose of this work is to preliminarily investigate the surface structure of poly(methacrylate)/poly(styrene-co-acrylonitrile)(SAN) blend thin films cast from tetrahydrofuran solution by contact angle measurements. The main questions investigated in this work are: (1) relation between the composition of the surface and the bulk, (2) the extent of surface enrichment of the lower surface free energy component, (3) the change of the surface composition corresponding to the change in the degree of mixing in the bulk, and (4) the effect of alkyl group on the surface structure.

Keywords: surface free energies, surface compositions, poly(methacrylate), poly(styrene-co-acrylonitrile), blends

INTRODUCTION

The surface structure of polymer blends has been attracting much interest from both theoretical and practical viewpoints, since many technologically important properties of polymer blends are controlled by the surface composition of the blend. Surface enrichment by the component of lower surface energy has been demonstrated in several studies[1,2].

Surface segregation in polymer blends reflects a balance of surface forces and bulk mixing thermodynamics, and some theoretical descriptions have been proposed which consider this balance in terms of a mean-field formalism[3]. Preferential surface enrichment has been documented by surface tension, contact angle, and X-ray photoelectron spectroscopy(XPS) measurements on several multicomponent polymeric systems[1-4].

In this work, we preliminarily investigated the surface structure of

poly(methacrylate)(PMA)/poly(styrene-co-acrylonitrile)(SAN) blend thin films cast from tetrahydrofuran(THF) solution by contact angle measurements.

EXPERIMENTAL

Table 1 lists the characteristics of the polymers used in this study along with the sources; Poly(methyl methacrylate)(PMMA), ply(n-propyl methacrylate)(PnPMA), and poly(n-butyl methacrylate) (PnBMA), and Poly(styrene-co-acrylonitrile) (SAN) of 20.3wt% acrylonitrile (AN) composition. The polymers were used as received. The molecular weight of the polymers were measured using a gel permeation chromatography (Waters 244). PS was used as the standard for calibration. PMA/SAN blends were prepared by spin coating from 10wt% THF solution of the blends onto a cover glass spun at 300rpm for 30s. The spin-coated specimens were dried slowly in a glass plate at a room temperature and then kept in a vacuum oven to constant weight at 60℃. The blend composition was 1/1 by weight. The temperature at which phase separation occurred on heating(cloud point) for blends exhibiting lower critical solution temperature (LCST) behavior was obtained by light scattering as described elsewhere[4]. The static contact angle of water and ethylene glycol onto the surface of samples was measured using a Kyowa contact angle meter. Twenty measurements were averaged. The surface free energy of sample films was calculated by the Owens' Method[5]. Table 1 also lists surface tensions and densities of polymers used in this study. The density was measured by the dilatometric method.

Table 1. Characteristics of Polymers used in this study

Polymer	Molecular weight	surface tension(dyne/cm^2)	density(g/cm^3)	Source
PMMA	Mn=12,510 Mw=24,380	40.06	1.190	Aldrich
PnPMA	Mn=92,550 Mw=142,650	35.24	1.080	Sp2*
PnBMA	Mn=83,870 Mw=146,860	33.26	1.080	Sp2
SAN	Mn=39,260 Mw=91,100	44.57	1.072	Asahi

* Sp2; Scientific Polymer Product Inc.

RESULTS AND DISCUSSION

Table 2 shows the cloud points of PMA/SAN blends. The values of the cloud point decrease as the length of the alkyl group in the PMA increases. The strength of the net interaction of PMA with SAN appears to follow the order PMMA>PnPMA>PnBMA or becomes weaker as the alkyl side chain becomes longer or bulkier such that PnBMA is not miscible with SAN at room temperature.

Table 2. Clould points of PMA/SAN blends

Blends	cloud point (°C)
PMMA/SAN	331
PnPMA/SAN	180
PnBMA/SAN	20

The surface fraction of PMA (f_{PMA}) was estimated by assuming that the surface free energy (γ) of the blend was proportional to the fractional surface coverage of each constituent[3].

Figure 1 shows that surface enrichment by the component of lower surface energy(PMMA) is observed for the PMMA/SAN blends. At the air-polymer interface the surface energy is an important component of the total free energy of the system which consists of three terms: the entropy of mixing, the interaction energy between polymer segments, and the surface energy. The preferential presence of the lower surface energy component at the interface is the result of the minimization of the total free energy of the system[1].

Table 3 shows that for the PMA/SAN blends, the surface weight fraction of PMA increases with increasing alkyl group. The lower the

Table 3. Surface compositions for PMA/SAN blends

Blends	Surface tension (dyne/cm^2)	Surface fraction of PMA (f_{PMA})	Weight fraction of PMA at surface
PMMA/SAN	51.0	0.676	0.698
PnPMA/SAN	37.5	0.758	0.759
PnBMA/SAN	35.5	0.802	0.803

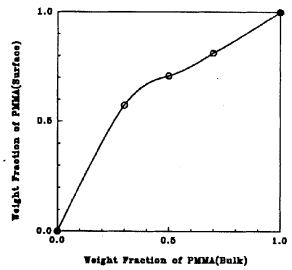

Figure 1. Surface weight fraction versus bulk weight fraction of PMMA: PMMA/SAN blends.

degree of mixing in the bulk, the more component of lower surface energy(PMA) was observed at the surface. Finally, it was also found that the surface enrichment of PnPMA increases in PnPMA/SAN blends when they exhibited thermally-induced-phase-separation by heating above the LCST (i.e. at 210℃). Similar result was reported for the polystyrene(PS)/poly(vinyl methyl ether) (PVME) system[3], where the lower the degree of mixing in the bulk, the more component of lower surface energy(PVME) was observed at the surface.

Acknowledgment
The work was supported by the Center of Integrated Molecular Systems, POSTECH, Korea and the Brain Korea 21 Project in 2001.

References

[1] W.K. Lee, W.J. Cho, C.S.Ha, A. Takahara, and T .Kajiyama, *Polymer*, **36**, 6, 1229(1995).
[2] W.K. Lee, T. Tanaka, A.Takahara, T.Kajiyama, and C.S.Ha, *Bull. Kor.Chem. Soc.*, **18**, 9, 958(1997).
[3] D.H.K.Pan and W.M. Prest Jr, J. *Appl. Phys.*, 58(8), 2861(1985).
[4] C.S. Ha, W.K. Lee, W.J.Cho, T.Ougizawa, and T. Inoue, *Kor. Polym. J.*, **9**, 1, 66(2001).
[5] D.K. Owens and R.C. Wendt, *J. Appl. Polym. Sci.*, **14**, 185 (1970).