

Preparation of Flexible and Transparent SMA Films by Simple Composite with MBS Potential for Negative Birefringence Compensator

Guo-Li Yuan, Chen Liu, Peng Han, Wei Xie

School of the Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China

Received 2 March 2010; accepted 12 September 2010

DOI 10.1002/app.33402

Published online 1 December 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The brittleness of poly(styrene maleic anhydride) (SMA) was improved by compositing with elastic poly(methyl methacrylate-butadiene-styrene) (MBS) to develop it into optical film. Transparent and flexible SMA films were prepared, and the flexibility of them was checked by folding endurance test and folding bend. The transparency of SMAMBS films were proved by the transmittance and haze measurements. In actual view, the letters could be clearly observed while they were covered by prepared films. The thermal stability of them was confirmed by DSC and TGA analysis. These physical properties of films are comparable to that of polycarbonate

which is widely used as optical film. Besides of these, mechanical and fracture properties of them were found to be also suitable for this purpose. Furthermore, negative birefringence could be obtained by orientationally stretching them. Such results indicate that, films prepared from composites are competent for negative birefringence optical compensator in the field of liquid crystal display. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1837–1842, 2011

Key words: poly(styrene maleic anhydride); composite; flexibility; negative birefringence; optical film

INTRODUCTION

Optical polymers have been widely used as key materials for various optical devices, such as, lenses and functional films for liquid crystal displays (LCDs).¹ Especially, polymer films with intrinsically negative or positive birefringence have been studied as compensators for LCDs.^{2–4} Polymers owning styrene unites are ideally materials for such application because styrene is a typical compound unit with negative birefringence.⁵ Polystyrene tends to exhibit negative birefringence caused by the orientation of the chains during processing by injection-molding, extrusion, and drawing, thus regarded as an optically anisotropic material.^{5,6} Nevertheless, the application of polystyrene as LCDs compensator films is still limited due to its weak thermal stability. So,

copolymers have been developed to solve this problem.^{7,8}

As well known, the thermal stability of polystyrene could be greatly improved by copolymerization with maleic anhydride (MA).⁹ Styrene maleic anhydride (SMA) copolymers are commonly industrial materials due to their water-solubility, high functionality, low-solution viscosity, and water insensitivity. They are widely used in surface treatments and in the automotive industry.^{10–12} Besides of these, SMA is an optical polymer contributed from intrinsic properties of styrene units in copolymer.¹³ In other words, SMAs could own their intrinsically negative birefringence while a suitable mole ratio of styrene unites is introduced into polymer chains. So, SMA has been considered as optical materials for LCDs compensators instead of directly using polystyrene.¹³ While more MA units are introduced into SMA chains, the polymer films become very brittle and not suitable to be used as large area optical films. Thus, the safely mole ratio of MA in SMA should be high. To fit the application in LCDs, general consideration is that thermal stability of polymer films should be comparing to Polycarbonate (PC), which is typically optical material due to its thermal stability and flexibility.¹⁴ So, it is challenge to prepare flexible and thermally stable SMA films to improve their application as LCDs optical compensators. Although many methods has been reported to improved the strength of SMA, such as crosslinking

Correspondence to: G.-L. Yuan (yuangl@cugb.edu.cn).

Contract grant sponsor: Specialized Research Fund for the Doctoral Program of Higher Education; contract grant number: 20090022120001.

Contract grant sponsor: Fundamental Research Funds for the Central Universities; contract grant number: 2010ZY24.

Contract grant sponsor: Scientific Research Foundation for the Returned Overseas Chinese Scholars by State Education Ministry in China.

Journal of Applied Polymer Science, Vol. 120, 1837–1842 (2011)
© 2010 Wiley Periodicals, Inc.

and functional groups-grafting,^{15,16} composite is a simple and effective method to improve the mechanical properties including strength and flexibility.^{17,18}

Herein, we report to develop transparent and flexible SMA films with strong mechanical strength by simply compositing it with MBS (poly(methyl methacrylate-butadiene-styrene)), wherein SMA is well compatible with MBS under assistance of PMMA, which extends the application of SMA as optical film in the field of LCDs.

EXPERIMENTAL

Materials

Poly(styrene-maleic anhydride) (SMA, DyLark 332) and poly(methyl methacrylate-styrene-butadiene) (MBS-600) in particles were provided by Nova chemical and Toumen Corp, Japan. The mole ratio of St/Ma is 85/15 in SMA, which was confirmed by NMR. The average molar weight of SMA is M_w 152,000 and M_n 58,000. The weight percent of butadiene in MBS is $\sim 20\%$ (M/B/S 40/20/40). PMMA (poly(methyl methacrylate)) was industrial products purchased from Kureha Chemical in Japan with M_w more than 100,000. Polycarbonate film (ARTON) was the commercial optical film used in LCD produced by JSR Co. Japan. All other compounds, such as MEK (methyl ethyl ketone), were the products of Sinopharm Chemical Reagent Beijing Co., China.

Methods

In three cases, SMA, PMMA, and MBS solutions or dispersions were prepared in MEK. For example, SMA solution was prepared by dissolving it in MEK, and the weight percent of it in solution was set at 40%. Concentration of PMMA in MEK solution was set at 50%. At the same time, MBS was dispersed in MEK with 30% weight concentration and the particle size was checked to be less than 1 μm . The dissolving and dispersing process were carried out under heating and ultrasonic assistance. After mixing above three solutions under suitable ratio, a transparent solution could be obtained, and the concentration of evaporated residue was adjusted to 33% by MEK.

Preparation of films

The film was prepared with an auto-rolling casting machine. The thickness of film could be controlled by the distance between shutter and roller. Typically, the mixture solution was cast on PE film and moving through heating box at 80°C for 3 min. Then, the film was peeled off and set on stainless steel plate. To remove the rudimental solvent, film

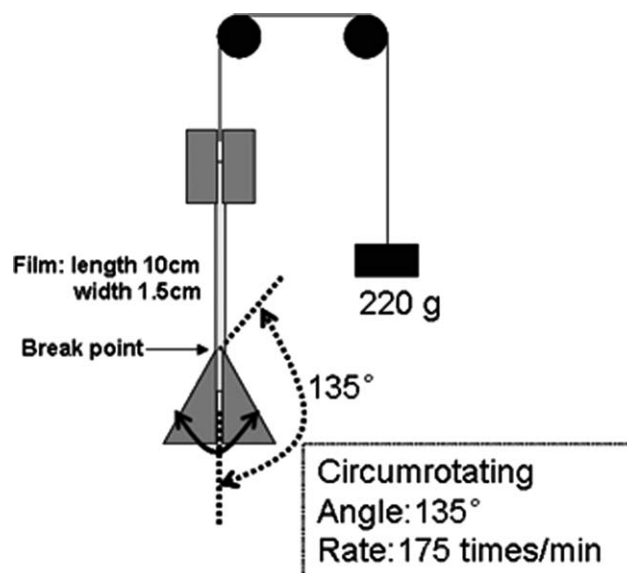


Figure 1 The sketch of machine for folding endurance measurement.

was heated in hot air cycle oven at 110°C (lower than the T_g of blend) for 45 min. The prepared films were used for characterization.

Characterization

Thermogravimetric analysis (TGA) of polymer films was carried with TGA-50H (SHMADZU) at a heating rate of 10°C/min in nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on DSC-6200 (SEIKO). Transmission and haze (550 nm) was measured with haze-meter (NDH1000, Nippon Denshoku Industries). The refractive index was performed according to standard of ASTM D542. Tensile and fracture tests were performed on MTS universal testing machine (Alliance RT/5) at room temperature. Birefringence was analyzed by optical birefringence analyzer (KOBRA-WR). Uniaxially or biaxially stretching films (2 cm \times 2 cm) were achieved with an auto-stretching machine at 130°C, and the draw ratio was set mechanically. Endurance was checked by MIT type folding endurance according to ASTM D2176 (sketch shown in Fig. 1).

RESULTS AND DISCUSSION

Flexibility and transparency

Although the mixture of SMA and MBS in MEK could be used to prepare film, the film is not so good, bad transmittance and hazy. After adding 10% weight of PMMA, transparent film could be obtained and PMMA served as dispersant. For this purpose, the blend of SMA/PMMA/MBS (SMAMBS) was prepared by changing the ratio of SMA and MBS while keeping the content of PMMA invariably. Certainly,

TABLE I
Optical Properties and the Folding Endurance of SMAMBS

	SMA (DyLark332)	SMAMBS-1	SMAMBS-2	SMAMBS-3	SMAMBS-4	PC ^a (ARTON)
SMA/PMMA/MBS (Weight %)	100/0/0	75/10/15	80/10/10	85/10/5	87.5/10/2.5	–
Weight Percent of Styrene (%)	85.8	0.71	0.73	0.75	0.76	0
Film Thickness (μm)	50	48	49	51	50	50
Transmittance % (550 nm)	92	90	93	91	92	93
Haze (550 nm)	0.77	1.82	0.9	0.81	0.78	0.80
Index of Refraction ^b	1.582	1.545	1.556	1.565	1.571	1.511
Folding Times at Breaking	<1	84	77	65	25	82

^a PC film was the commercial products of JSR.

^b Measurement according to ASTM D542.

the content of styrene units is necessary to develop it as optical film with negative birefringence. Some examples (SMAMBS-1,2,3,4) were selected and their physical properties are shown in Table I. As a contrast, some properties of commercial PC optical film (polycarbonate, ARTON) are also tested and shown in table, which has been widely used as optical film in liquid crystal display (LCD).¹⁹ For all of SMAMBS films, transmittances of them are over 90%. In folding endurance test, SMA film is very brittle and breaks less than 1 time. The folding endurance increases as increasing the ratio of MBS in composite. While the content of MBS increased into 15%, the film became very flexible which is competent to PC. However, the haze for it is rather high which retard it to be used as optical film. While the content of MBS in blend decreased into 2.5%, folding times for breaking dropped to 25, which is far lower than that of PC. While content of MBS was adjusted to 10% and 5% (SMAMBS 2, 3) respectively, the folding endurance is comparable to that of PC. Moreover, other physical properties are close to that of PC. So, SMAMBS-2 and

SMAMBS-3 are considered as the potential material for preparing optical film with negative birefringence.

Figure 2 is the image of SMAMBS-3 film covering on the typed letters, wherein white lines denote the size of film. As shown in image, the film is so transparent that the covered letters could be observed as clearly as that not covered. Such a result is contributed to 93% transmittance of the film. As discussed above, SMAMBSs own good flexibility which is comparing to that of PC. To get sensibly view, the film of SMAMBS-3 was fold by tweezers. As shown in Figure 3, the film is well bent at 180 degree and not rupture. Although the image is not shown here, SMA film without MBS rupture quickly after folding. Based on these, it is clear that flexibility of SMA is greatly improved after its compositing with MBS while keeping its transparency.

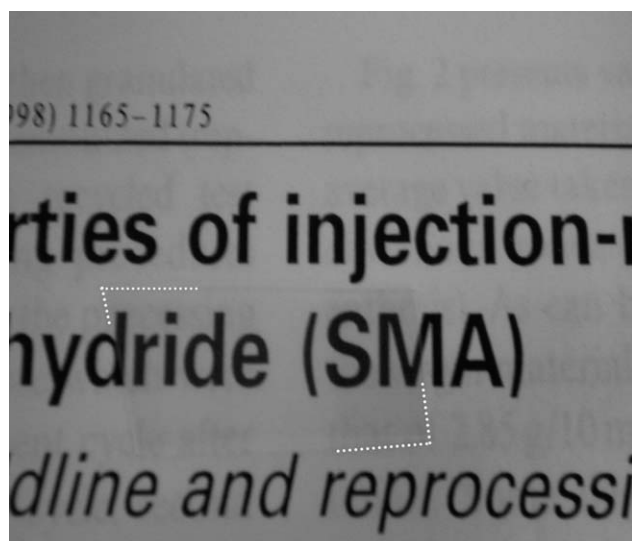


Figure 2 View of film covering words (edge of film in white line).

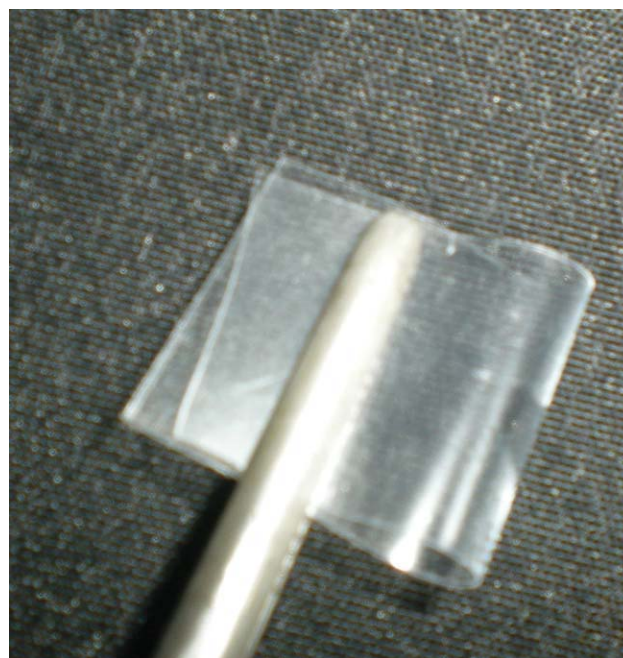


Figure 3 SMAMBS-3 film bent with tweezers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

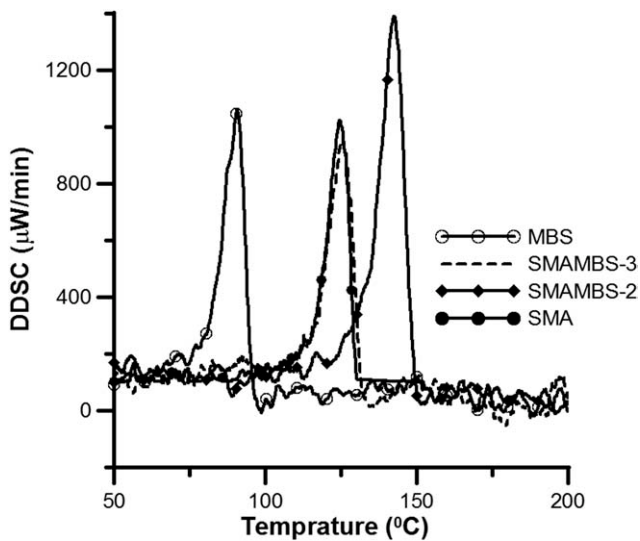


Figure 4 DDSC curves of SMA, MBS, and SMAMBSs.

Thermal properties

Figure 4 shows the DDSC curves of MBS, SMA, SMAMBS-2, and SMAMBS-3. As observed, T_g (glass transition temperature) of SMA is at 142.4°C and MBS at 90.7°C. As expected, T_g of SMAMBSs is shown in the middle of them, SMAMBS-2 at 124.4°C and SMAMBS-3 at 125.7°C, respectively. They are competent to that of PC, $\sim 120^\circ\text{C}$,² which is presumed to fit the requirement of optical film. Based on this point, thermal property of SMAMBS is suitable for the purpose. Figure 5 shows the TGA curves of these film samples. SMA is rather stable whether in environment of N_2 or air, which does not degrade until 350°C. MBS show different characterization, and it almost does not lose its weight until 350°C in N_2 while losing it at 300°C in air. After blending SMA and MBS, it seems that the thermal stability decreases as the ratio of MBS/SMA increasing in composite. SMAMBSs begin to lose their weight from $\sim 270^\circ\text{C}$. On the other hand, SMAMBSs show almost similar TG characters whether in N_2 or air. The possible reason is presumed that the major content of SMA in them dominates the thermal stability of SMAMBS. Comparing to SMA and MBS, the inferiority in thermal stability of SMAMBSs maybe originate from the in-continuous phase in blend and PMMA. Although there is a little drop in thermal stability of blend comparing to SMA, the degrading temperature of SMAMBSs are still over 250°C. Such a thermal stability is comparable against to that of PC.¹⁹

Mechanical and fracture properties

Three parameters were selected to observe the mechanical properties of SMAMBSs. The one is fracture elongation of films which indicates the degree of dis-

tortion in films suffering force. The others are fracture stress and tensile modulus which commonly account for the endurance of film against force. Fracture elongation of film is a very important parameter to evaluate its suitability to be applied as optical film. To keep clear view, the optical films should keep its shape and no distortion while suffering outside force, such as the tension force during the process of manufacturing optical products and the extrusion force during the using products. As shown in Table II, SMAMBS films show a little increase in fracture elongation, 1.88 and 2.49% respectively, comparing to that of SMA 1.68%. It is reasonable to believe that such an increase in elongation originates from composite with elastic MBS.

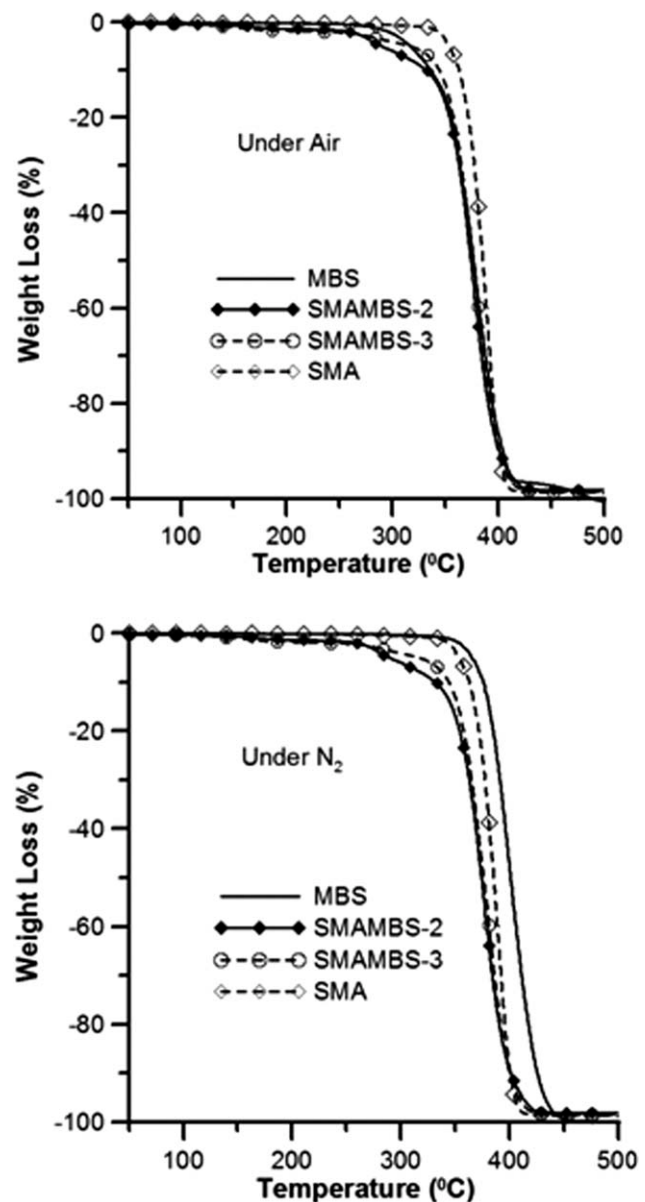


Figure 5 TG curves of SMA, MBS and SMAMBSs under air and nitrogen.

TABLE II
Mechanical and Fracture Properties of SMAMBS in Tensile Test^a

	Tensile modulus (GPa)	Fracture elongation (%)	Fracture stress (MPa)
SMA	2.65	1.68	46.8
SMAMBS-2	2.62	3.26	51.8
SMAMBS-3	2.65	2.89	47.4

^a The test performed at room temperature; Film: 1.0 cm width, 6.0 cm length, 50 μm thickness.

On the other hand, the fracture stress is another very important parameter to evaluate its suitability to be applied as optical film because a popular used optical product has to own a certain strength withstanding outside force.^{20,21} After blending with MBS, SMAMBSs show some improvement in fracture stress from 46.8 MPa to 51.8 MPa (Table II). Although mechanism for such an improvement is not clear, it is presumed that flexibility helped to prepare a better film than brittle one. As a result, the better prepared SMAMBS films show higher fracture stress than that of SMA.

Orientalional draw

The SEM images (Fig. 6) prove that MBS is well dispersed in SMA as less than 1 μm domains. As mentioned above, common SMA film does not show negative birefringence due to the random arrangement of polymer chains. To get a negative birefringence SMA film, the styrene units have to be orientated by stretching the film. So, the orientational stretch of SMAMBS-3 film was performed at the temperature over the Tg of material. Although the orientation of styrene units cannot be observed by SEM, the orientation of MBS domains could be clearly observed. After 2 times uniaxially drawing, indefinite shape of MBS domains became into oval shape and re-arranged into one direction along extension axis [Fig. 6(B)]. It is suggested that MBS domains are synchronously stretched with the extension of SMA. Nevertheless, no gaps or interspaces were observed between SMA matrix and MBS domains. Figure 6(C) shows the image of SMAMBS-3 after diaxial extension while the draw ratio was set at 2. Except a little increase in size of domains, no gaps were found between matrix and domains. These images illustrated that MBSs were well composited with SMA matrix. Thermal extension seems unlikely to make phase separation between MBS and SMA. Although orientational stretch of SMA film has been tried, it was difficult to get a good film because it is so easy to break and disrepair.

Orientalional birefringence

Birefringence is the division of a ray of light into two rays when it passes through an optically aniso-

tropic material, depending on the polarization of the light. Two different refractive indices are assigned to the material for different polarizations. In the case of uniaxially drawn polymer samples, the orientational birefringence Δn is defined as $\Delta n = n_r - n_t$, where

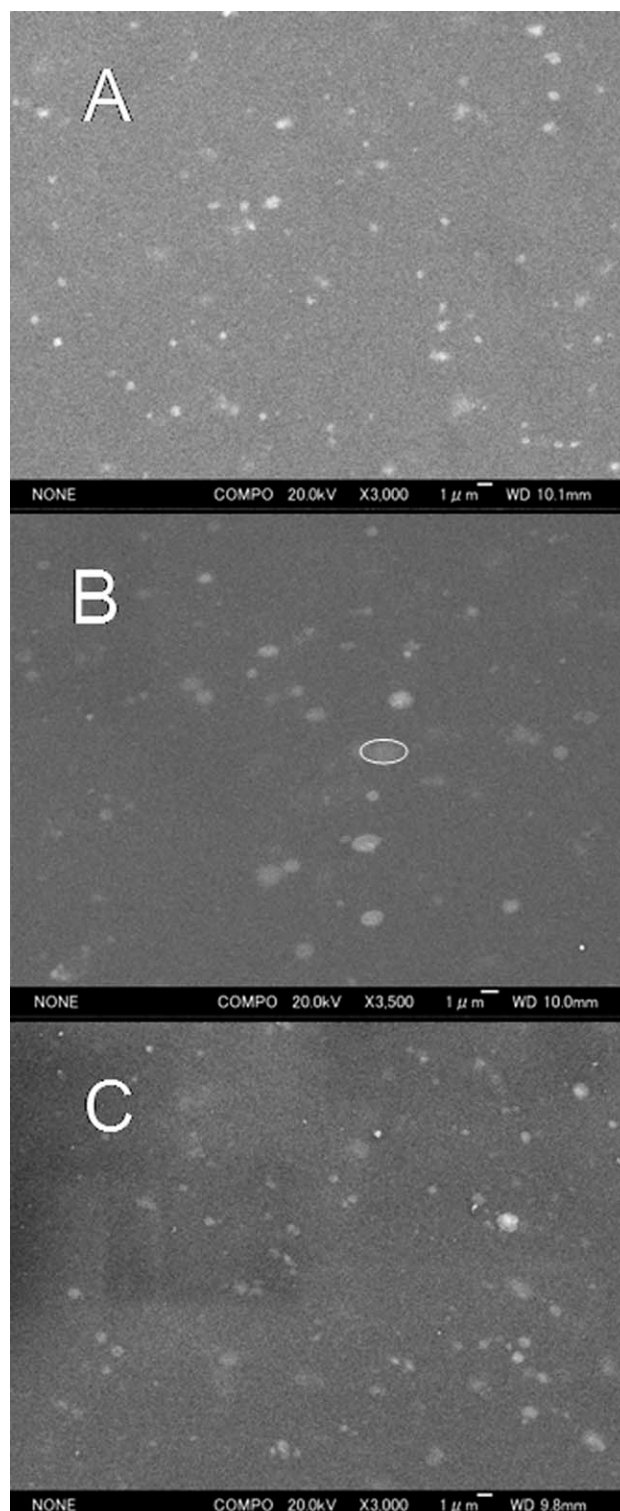


Figure 6 SEM images of SMAMBS-3 film (A) original prepared, (B) 2 times uniaxially drawn (white line shipping oval MBS), (C) 2 times biaxially drawn.

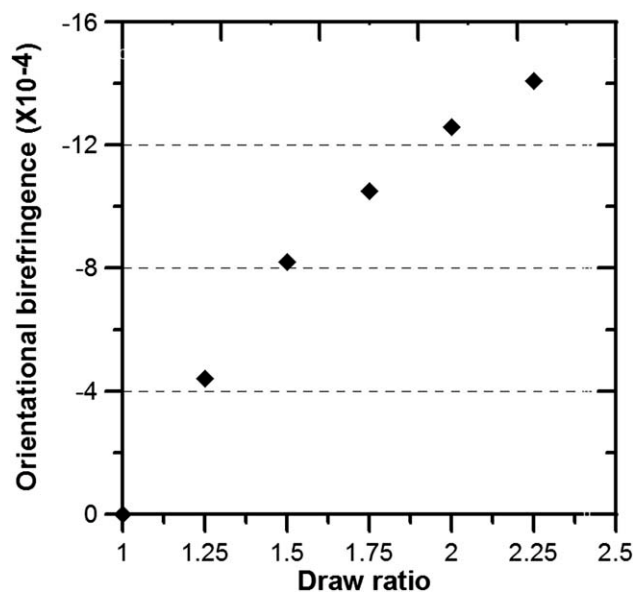


Figure 7 Orientational birefringence of SMAMBS-3 film with respect to draw ratio.

n_r and n_t are the refractive indices of the parallel and perpendicular direction to the drawing direction, respectively. So, the light passes through the material with birefringence Δn and thickness d , the retardation R is given by $R = \Delta n d$.

The orientational birefringence of SMAMBS-3 film by uniaxially heated-drawn is shown in Figure 7. The data were gained at 550 nm with KOBRA-WR. It is observed that the absolute value of birefringence increased with draw ratio increasing. Although there is not linearity relationship between birefringence value and draw ratio. At range between 1 and 2.5, draw ratios precisely control birefringence of the film. It is suggested that, the draw ratios definitively affect the degree of orientation styrene units in chains. While higher draw ratio provide higher orientation, higher orientation offers higher birefringence. The negative orientational birefringence provides a proof for SMAMBS films to be used as optical compensator films, such as in the field of LCDs.²² Referring to application of SMAMBS in LCDs, Toyomasu et al. showed a well possible example using negative birefringence film as optical compensator films to improve viewing angles of LCDs.⁷ Because of the structure of LCDs, optical anisotropy is inescapability and yielded positive birefringence depends on the viewing angles. As a result, the viewing angles influence the quality of the picture in LCDs. So, applying retardation films with negative birefringence is a significant technical method to improve viewing angles of LCDs.

CONCLUSIONS

Transparent and flexible SMA films were prepared by compositing it with MBS, and the suitable ratio of MBS was found to be 5–10% in weight. The flexibility of films was checked by folding endurance test and the folding bent. The transmittance of films was over 90% and haze was less than 1. In actual view, typed letters could be clearly observed while they are covered by prepared films. The thermal stability of films was detected by DSC and TGA, which shows T_g at $\sim 120^\circ\text{C}$ and not decomposes until to $\sim 300^\circ\text{C}$. All of these are comparable to that of commercial polycarbonate optical films. Mechanical and fracture properties of films were also performed by tensile and fracture tests. Besides of these, SEM images suggested that the films were suitable to be uniaxially or biaxially stretched without phase separation. Consequently, the orientational birefringence indicates that SMAMBS films are competent for negative birefringence optical compensator.

References

- Zhou, W. J.; Diehl, C.; Murray, D.; Koppi, K. A.; Hahn, S.; Wu, S. T. *J Soc Inform Disp* 2010, 18, 66.
- Yun, J. H.; Kuboyama, K.; Ougizawa, T. *Polymer* 2006, 47, 1715.
- Yamaguchi, M.; Okada, K.; Manaf, M. E. A.; Shiroyama, Y.; Iwasaki, T.; Okamoto, K. *Macromolecules* 2009, 42, 9034.
- Rizzo, P.; Albonia, A. R.; Guerra, G. *Macromol Chem Phys* 2009, 210, 2148.
- De Francesco, A.; Duckett, R. A. *Polymer* 2004, 45, 4297.
- De Francesco, A.; Duckett, R. A. *Polymer* 2004, 45, 8005.
- Toyomasu, S.; Ikai, Y.; Harunari, T.; Doi, T.; Yamakawa, H. *Tosoh Res Technol Rev* 2004, 48, 23.
- Li, F.; Harris, W.; Cheng, S. Z. D. *Polymer* 1996, 37, 5321.
- Shaghghi, S.; Mahdavian, A. R. *J Polym Res* 2006, 13, 413.
- Belkhiria, S.; Meyer, T.; Renken, A. *Science* 1994, 49, 4981.
- Suzuki, F.; Nakane, K.; Hata, Y. *J Membr Sci* 1995, 104, 283.
- Fang, W. J.; Cai, Y. J.; Chen, X. P.; Su, R. M.; Chen, T.; Xia, N. S.; Li, L.; Yang, Q. L.; Han, J. H.; Han, S. F. *Bioorg Med Chem Lett* 2009, 1903, 19.
- Kuboyama, K.; Kuroda, T.; Ougizawa, T. *Koubunshi Ronbunshu (Japan)* 2004, 61, 89.
- Moon, I. K.; Chun, H. *J Sol-Gel Sci Technol* 2009, 52, 49.
- Samyna, C.; Verbiest, T.; Kesters, E.; Van den Broeck, K.; Van Beylen, M.; Persoons, A. *Polymer* 2000, 41, 6049.
- Mulder, F. M.; Heinen, W.; van Duin, M.; Lugtenburg, J.; De Groot, H. J. M. *Macromolecules* 2000, 33, 5544.
- Stretz, H. A.; Cassidy, P. E.; Paul, D. R. *Science* 1999, 74, 1508.
- Li, R.; Yu, W.; Zhou, C. *Polym Bull* 2006, 56, 455.
- ARTON Department of Tsukuba Lab, *JSR Techn Rev* 2003, 110, 27.
- Chrysostomou, A.; Hashemi, S. *J Mater Sci* 1998, 33, 4491.
- Chrysostomou, A.; Hashemi, S. *J Mater Sci* 1998, 33, 1165.
- Tagaya, A.; Ohkita, H.; Mukoh, M.; Sakaguchi, R.; Yasuhiro, K. *Science* 2003, 301, 812.