

Compatibility studies of bromo butyl and polychloroprene elastomer blends through atomic force microscopy

K N Pandey*, Vishal Verma, Pratibha Singh & Vijai Kumar

Central Institute of Plastics Engineering and Technology, Lucknow (CIPET), India

*E-mail: knpandey09@gmail.com

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In order to determine and optimize structure property relationship in polymer blends, knowledge of microscopic morphology is essential. However, much of this microscopic morphology and physical property information work have not been yet done and is not readily available particularly using conventional characterization techniques. In the present study, the capability of topographic and force modulation or phase atomic force microscopy (AFM) for determining the detailed microstructure of bromo butyl (BIIR) and polychloroprene (CR) blends is evaluated. The modulation contrast obtained in this analysis of the blends allows distinguishing a phase and related morphology with ease and good specificity. AFM studies of the BIIR and CR blends in the presence and absence of compatibilizer chlorinated polyethylene (CPE) reveal that the CPE is acting as an efficient compatibilizer. In the presence of CPE as compatibilizer in the blends, the topo image demonstrates the single phase characteristics. Phase image indicates the uniformity in the phase distribution and has been observed in histogram plot which ultimately results in reduction of mean and rms deviations.

Keywords: Polychloroprene, Bromobutyl rubber, Chlorinated polyethylene, Compatibilizer, Atomic force microscopy

1 Introduction

It is a common practice to blend two elastomers together even if they are thermodynamically incompatible or possess different levels of polarity or solubility. The use of polymer blends is becoming an important factor in satisfying the needs of specific sectors in polymer industries^{1,2}. Blending of polymers provides an important route to combine properties of blend component and thus give rise to new materials with an optimized performance^{3,4}. Polymer blends frequently meet performance demands that cannot be satisfied by the individual components of the blends. The majority of polymer pairs are immiscible from the thermodynamic point of view resulting in inferior mechanical properties⁵⁻⁸. Many researchers tried their level best to reduce phase separation and enhance interfacial adhesion⁹⁻¹². Reduction of phase separation and enhancement of interfacial adhesion can be achieved by the addition of a suitable compatibilizer which has the potential to generate at least a technological compatibilization. The distinct advantage of adding a compatibilizer into an immiscible rubber-rubber blends is to economize the mixing process for the graded addition of the component parts to extend the characteristics regime of the individual rubber.

Bromo butyl rubber (BIIR) possess unique combination of properties e.g. excellent in

permeability, good flex, good weatherability and low thermal stability. These properties make it a preferred material for tyre inner liners and curing bleeders. Because of the ozone resistance, weather resistance, oils and chemical resistance, outstanding physical toughness, flame retardant, high thermal stability of polychloroprene rubber (CR), its blends with BIIR would be attractive, provided they are compatible. Blends based on CR and BIIR are likely to be important in defense services for developing various rubber products with the above properties and characteristics. Various sophisticated instrumental methods, including thermal, microscopy, spectroscopy and processing techniques, to characterize rubber-rubber blends and compatibility have been discussed by Setua *et al*³. and Pandey *et al*⁸.

The main objective of the present work is to explore the compatibility of BIIR/CR by the addition of suitable compatibilizer with the help of Atomic Force Microscopy (AFM). Generally, SEM or Low Vacuum (LV) SEM are used to obtain morphological information regarding the polymer surface and the cryogenically fractured cross-sectional face^{13,14}. The recent development of AFM has opened a new dimension for determining polymer morphology with nanometer or better spatial resolution¹⁵⁻¹⁷. Various modes of operations (e.g. contact, tapping and lateral force) have been used successfully to view the

crystallites, nanofibrillar structures, morphology of elastomers and thermoplastic block co-polymer and compositional maps of elastomers and elastomers-toughened thermoset blends^{18,19}. Besides this, AFM is also capable of analyzing structural features of nanotube-polymer association in poly thiophene based nanocomposites²⁰.

2 Experimental Details

Bromo isobutylene-co-isoprene/bromo butyl rubber (BIIR) from Polysar, Canada, grade X2, polychloroprene/neoprene (CR) from DuPont, USA grade W-M1 and chlorinated polyethylene rubber (CPE) from M/s Dow Chemical, Plaquemine, LA, USA, grade Tyrin CM 0316 having chlorine content 36 mol% are used in this study. Other chemical like paraffin wax used in this study was obtained from M/s BDH (India) Pvt Ltd, analytical grade stearic acid, MgO, ZnO and sulphur used in this study were obtained from M/s E-Merck, Germany, analytical grade PBNA, MBTS and TMTD used in this study were obtained from M/s Bayer, Germany and analytical grade Na-22 used in this study was obtained from M/s DuPont, USA.

Neoprene and butyl rubbers were masticated separately and then mixed together. Mixing was carried out in a conventional laboratory open mill (150×330 mm) at 30-40°C according to ASTM designation D15-70. Different ingredients were added by careful control of temperature, nip gap, time of mastication and uniform cutting operation. The compounding ingredients were then added in the blends as per ASTM designation D 15-62 T. Optimum cure time at 160°C for the mixes was obtained by using rheometer. Mixes were vulcanized to their respective optimum cure times at 160°C for 15 min and at 4.5 MPa pressure in hydraulic press. The compatibilizer CPE was first compounded with BIIR at 10 wt. % content to prepare a master batch in two roll mill at 80°C and subsequently mixed with masticated CR. The compounding formulation of BIIR/ CR blends with and without compatibilizer is presented in Table 1.

For tensile test, universal testing machine (UTM) of a constant rate of cross head movement at a speed of 3 mm/min is used. Tensile tests were carried as per ASTM method D 3039-76 at room temperature. The tear strength was measured using an unnotched 90° angled test specimen according to ASTM method D 624. Tear tests were carried out in an universal testing machine and at a stretching rate of 550 cm/min.

Abrasion loss of the moulded samples was measured by a Du Pont Croydon Abrasion Tester Make S W Wallace & Co, England according to ASTM method D1630. The specimens were abraded for 2 min and the abrasion loss was calculated in terms of volume loss per hour. Shore A hardness was measured according to ASTM D 676-52 T. The term hardness has been applied to scratch resistance and to rebound resilience.

Atomic Force Microscopy (AFM) images of the blends were obtained in an intermittent contact mode at 8 Hz in Quesant model Q Scope 250 of Quesant Inst. Corp., Agoura Hills, CA, USA. The surface required for the AFM study was prepared by fracturing the vulcanized rubber strips, cut-out from the molded sheets at -196°C (under liquid nitrogen) followed by microtoming at -100°C. AFM imaging was carried out using a scanning head of 40 µm×20 µm. Topography, phase imaging and histogram plots were recorded simultaneously.

3 Results and Discussion

The compatibilizing effect of CPE has been studied having blend ratio of 60:40 of BIIR and CR. As observed from Table 2 that the addition of CPE on the

Table 1 — Compounding formulation of BIIR/CR blends without and with compatibilizers

Ingredients	Content of Mix (part by weight)	
	Blend without compatibilizer	Blend with CPE
Bromobutyl rubber (BIIR)	60.0	60.0
Polychloroprene rubber (CR)	40.0	40.0
Chlorinated polyethylene (CPE)	--	5.0
Paraffin wax	5.0	5.0
Stearic acid	1.0	1.0
PBNA	1.0	1.0
MgO	4.0	4.0
ZnO	5.0	5.0
Sulphur	1.5	1.5
MBTS	1.5	1.5
Na-22	0.3	0.3
TMTD	1.5	1.5

Table 2 — Physico-mechanical properties of BIIR/CR blends without and with compatibilizer

Property	Blend type : BIIR/CR (60:40)	
	Blend without compatibilizer	Blend with compatibilizer (CPE)
Tensile strength, kg/cm ²	48.0	97.1
Modulus (300%), kg/cm ²	13.8	18.2
Elongation at break (%)	6.50	8.75
Tear strength, kg/cm.	13.0	15.5
Hardness, shore A	38.0	44.0

blend of BIIR/CR (60:40), the tensile strength increased about 100% accompanied by increased modulus, tear strength, hardness and elongation at break. These observations clearly revealed that the 60:40 original blend ratio of BIIR/CR probably needs more halogen groups, which were compensated by the additional CPE added as compatibilizer. The better effectiveness of CPE as compatibilizer may be due to higher percentage of halogen content of CPE, which probably enhanced the interfacial adhesion between two base polymers, because CPE is highly amorphous and rubbery in nature.

AFM photograph of the pure bromo butyl, pure polychloroprene, their 60:40 blends and 60:40 blends in the presence of CPE are shown in [Figs 1(a, b and c), 2(a, b and c), 3(a, b and c) and 4(a, b and c)], respectively. The subscripts a, b and c are corresponding to their topo image, phase image and the histogram, respectively. The surface topography of the pure bromo butyl clearly revealed the single phase system [Fig. (1a)], however, for pure polychloroprene rubber certain amount of crystalline domains are clearly visible [Fig. (2a)]. These observations are corroborated by their phase images in the Figs (1b, 2b). The histograms of both the pure rubbers [Figs (1c and 2c)] clearly indicate the narrow distribution in case of bromo butyl having larger particle size as compared to wider distribution accompanied by the lower particle size in the case of polychloroprene rubber. In case of 60:40 blends of bromo butyl and poly-chloroprene rubber, the topo

image [Fig. (3a)] suggests the distinct two blends as confirmed by the phase image [Fig. (3b)]. However, the histogram [Fig. (3c)] suggests the comparatively uniform wider particle distribution accompanied by the decreased particle size. This may be due to certain amount of intermolecular interaction making the particle size distribution comparatively uniform. In the presence of CPE as compatibilizer in the blends, the topo image (Fig. 4a) suggests the single phase characteristics. Phase image [Fig. (4b)] also suggests

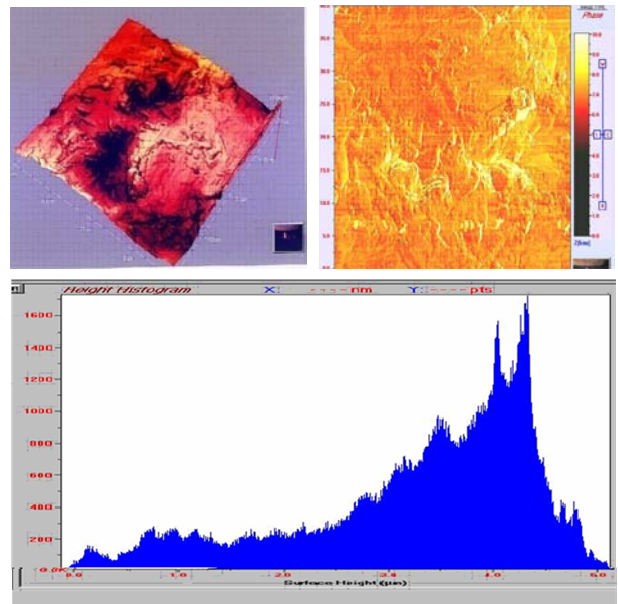


Fig. 2 — AFM photos of (a) Surface topography, (b) Phase image and (c) Histogram plot of CR

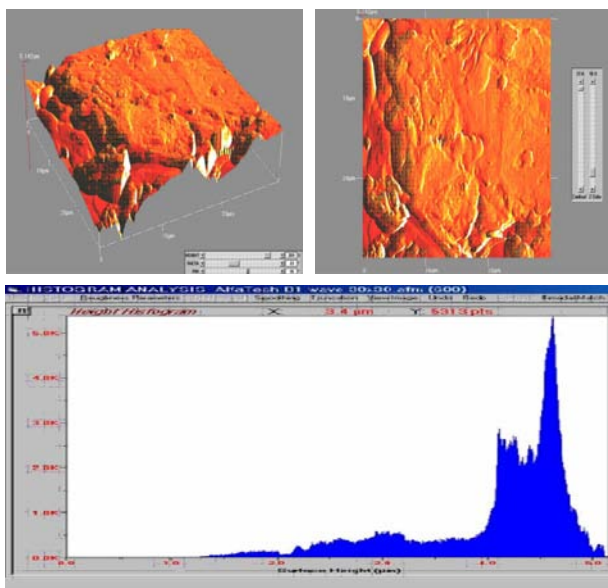


Fig. 1 — AFM photos of (a) Surface topography, (b) Phase image and (c) Histogram plot of BIIR

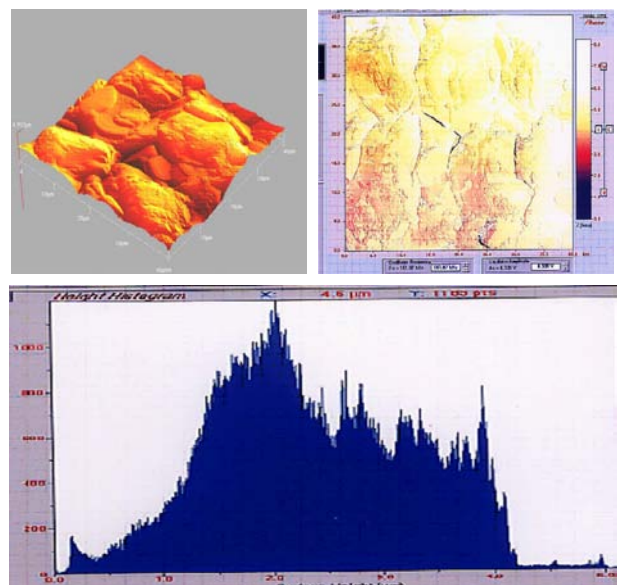


Fig. 3 — AFM photos of (a) Surface topography, (b) Phase image and (c) Histogram plot of BIIR: CR blend without compatibilizer

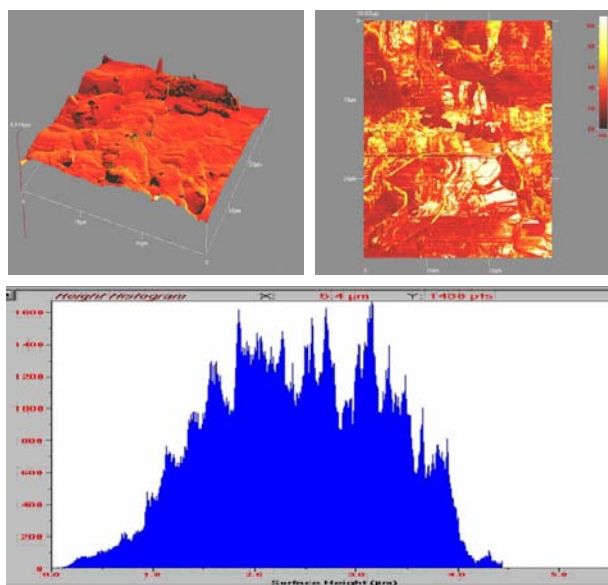


Fig. 4 — AFM photos of (a) Surface topography, (b) Phase image and (c) Histogram plot of BIIR: CR blend with CPE as compatibilizer

the uniformity in the phase distribution. However, the presence of CPE has widened the particle size distribution with much reduced particle size [Fig (4c)] as evident from drastic reduction in rms and mean deviations. These observations clearly demonstrate that CPE may be an efficient compatibilizer for BIIR/CR blend system.

4 Conclusions

AFM studies show that CPE acts as an efficient compatibilizer for BIIR/CR blends. These results are found to be in good agreement with the earlier studies conducted with the aid of thermal characterization techniques²¹. Thus, it is concluded that the efficacy of CPE as a compatibilizer of the blend system is

excellent with improved physico-mechanical properties and thermal stability.

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