Preparation of Cross-linked Asymmetric Membrane and Control of Its Morphology and Mechanical Property

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Abstract: Polystyrene-co-divinylbenzene (PS-co-DVB) asymmetric membranes were prepared. In order to control their structure and mechanical properties the degree of cross-linking and the composition of casting solution were varied. The rubber added PS-DVB membranes was also prepared to overcome the mechanical limitation of cross-linked membrane, and their mechanical properties were investigated. It was revealed that the concentration of polymer in the casting solution affected the determination of skin formation. When the PS-co-DVB membrane consists of styrene-butadiene (SB) rubber or liquid polybutadiene (PBD), the structures formed showed that the PS content in the PS/DVB system played an important role in determining the porous sublayer structure.

Keywords: polystyrene-divinylbenzene, asymmetric membrane, SB rubber, polybutadiene

1. Introduction

Membranes are rapidly gaining an important place in chemical technology, especially for separation processes [1-4]. Conventional membranes made from linear polymers are susceptible to chemical attack, and one avenue to improve resistance is to employ cross-linked polymers.

Reverse osmosis can be briefly described as a process that uses a semipermeable membrane [5], which allows solvent permeation or transport but acts as a highly effective barrier to the passage of dissolved and suspended substances. The direction of solvent flow is determined by its chemical potential, which is a function of pressure, temperature, and the concentration of dissolved solids (Reid, 1966) [6].

Although separation of solutions by R. O. is applicable for both aqueous and organic solutions, R. O. membranes have been used most extensively for water

desalination and purification. The first work in R. O. for water-desalting was undertaken by C. E. Reid and his co-works in the late-1950s (Reid and Spencer, 1960; Breton and Reid, 1959; Reid and Kuppers, 1959) [7-9]. They demonstrated that cellulose acetate was highly selective in passing water and rejecting salt, but their membranes were too thick to yield practical fluxes. In the early 1960s, Loeb and Sourirajan at UCLA (1962) [10] then discovered a modified casting technique to achieve an asymmetric cellulose acetate membrane. This discovery permitted R. O. to become the practical process it is today, and all commercial membranes now use the asymmetric structure in one form or another.

It is well known that CA membranes have excellent salt rejection and high flow rate. Nonetheless, the preparation of new types of membranes from other synthetic polymers has been investigated extensively due to the limitations of cellulose membranes (Nishimura, 1979; Stannett *et al.*, 1977; Kimura-Yeh *et al.*, 1972) [1,2,11]. Cellulose membranes typically exhibited

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Table 1. The Composition of Casting Solutions

Sample code	DVB	PS	Styrene	NMP	Benzoin	SBS Rubber	PBD
S1	2%	25.0%	46.1%	26.4%	0.5%	-	-
S2	5%	25.0%	44.2%	25.3%	0.5%	-	-
S3	10%	25.0%	41.0%	23.5%	0.5%	-	-
S4	20%	25.0%	35.0%	19.5%	0.5%	-	-
S5	10%	22.5%	41.0%	23.5%	0.5%	2.5%	-
S6	10%	22.5%	41.0%	23.5%	0.5%	-	2.5%

flux decline, and have a limited resistance to chemical and biological attack (Motomura and Taniguchi, 1981; Reese and Mandels, 1971) [12,13]. Thus, cellulose membranes are usually operated using chlorinated feed water to prevent such attack. In addition, cellulosic R. O. membranes are easily degraded in solutions with pH greater than 6.5, due to the hydrolysis of its acetyl group (Channabasappa, 1976) [14]. These membranes have also shown "pore compaction" after prolonged exposure to high pressure (Orofino et al., 1970) [15].

A new class of membrane materials and fabrication techniques has emerged to reduce the previous limitations. Fujita and Soane (1988) have formed a cross-linked asymmetric/porous membrane with PS [16]. They developed a technique to prepare asymmetric membranes from PS-co-DVB with ultraviolet light. In essence, partial polymerization and photo cross-linking first occurs, followed by phase inversion to develop a semi-stable porous cross-section. Since cross-linked copolymers of styrene and DVB have been used for the preparation of ion-exchange resins or in gel permeation chromatography, they must be mechanically stable, having to withstand the stresses arising from the rapid ionic concentration fluctuations encountered during ion-exchange regeneration ("osmotic shock").

In this stduy, we prepared asymmetric PS membranes cross-linked with DVB. In order to control the morphology and mechanical property of prepared PS-co-DVB membrane rubber added PS-co-DVB membranes were prepared also. The effect of the degree of cross-linking of prepared membranes on the morphology and mechanical property was also investigated.
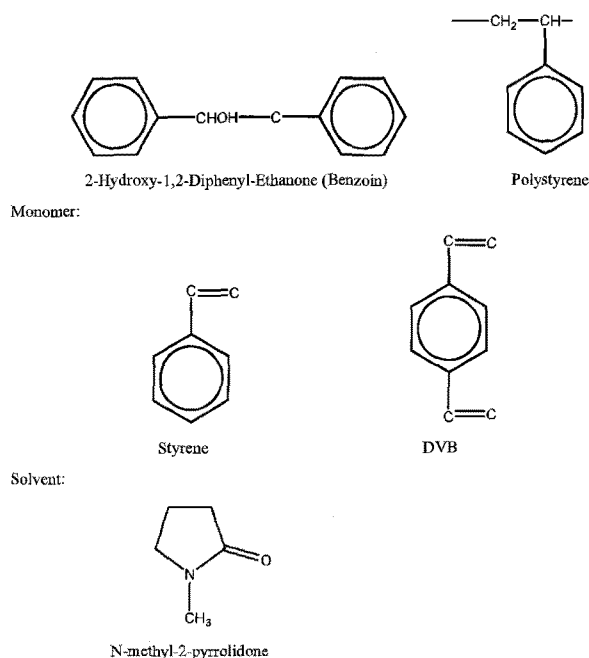

Fig. 1. Components of the casting solution.

2. Experimental

2.1. Materials Preparation

PS with an M_N of about 260,000 was used, as supplied by Chemplex. Styrene monomer (Ajax) and DVB monomer (Polyscience) were treated with "Drierite" in order to remove the inhibitor t-butylcatechol. The DVB monomer was stated to be 55 to 60% active. SB rubber (Solprene 1205) was obtained from Phillips Chemical Co. and contains 25 wt% styrene. It is a diblock copolymer with a stated M_N of 83,000. The liquid PBD obtained from Polysciences has 85% vinyl 1, 2, groups and a molecular wight of 1,000.

The procedure was to make casting solutions containing PS, styrene monomer, DVB cross-linker, benzoin
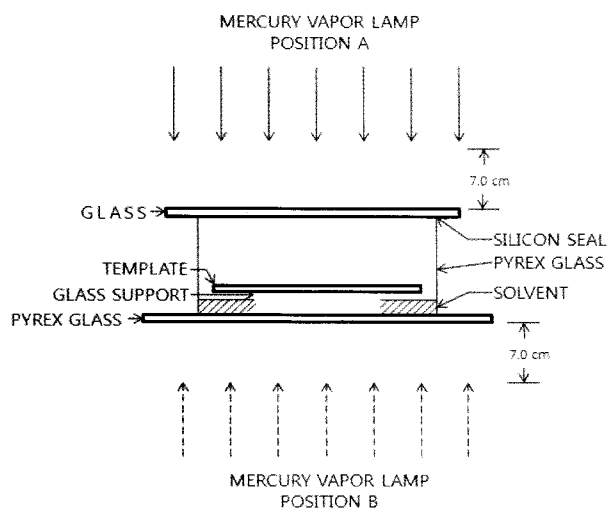
Fig. 2. Experimental set up.

photoinitiator, and N-methyl-2-pyrrolidone diluent. Their chemical structures are shown in Fig. 1. PBD or SBS rubber was added to the same casting solutions at an initial concentration of 2.5%wt/wt. The composition of all casting solutions are listed in Table 1. These solutions were stirred continuously 24 hrs in darkness, and then vacuum filtered through a glass sinter at room temperature to remove particulate matter, reduce bubbles and eliminate undissolved polymer. The solutions were then spread with a glass rod onto a glass plate framed with a 75 μm thick PTFE sheet to give a 5 cm × 5 cm liquid film. The cast solution was then placed in a 12.5 cm diameter glass petri dish with solvent underneath. After exposure to ultraviolet light for 24 hrs, a partially cross-linked sol formed. Solvent evaporation prior to polymer coagulation was prevented by extra solvent contained in the petri dish. The partially polymerized films were then coagulated in methanol containing benzoin. The non-solvent bath was exposed to U.V. light for an additional 24 hrs to form the final structure. The U.V. light was provided by a two 20 watt mercury vapor lamps (Sankyo Denki, GL 20SE), located approximately 7 cm from the film. The experimental set up is illustrated in Fig. 2. The membranes produced were rinsed with water and stored in water at room temperature. For scanning electron microscopy and modification studies with sulfuric acid, membranes

were carefully dried at room temperature in a vacuum oven for at least on week.

2.2. Electron Microscopy

The dried membranes were fractured in the liquid nitrogen to view the structures with scanning electron microscopy (SEM). For SEM, Jeol JXA-840 and Cambridge 3600 were used. A "Polaron" sputter coater was used to coat the samples with gold-palladium, giving a coation thickness of 30 nm.

2.3. Mechanical Testing

The tensile strengths and elongations at break were measured according to the ASTM method (D 882-79) with an Instron Model 1115 tensile tester, at room temperature. A crosshead speed of 0.5 cm/min was used. Samples approximately 2 cm wide and 4~5 cm long, and an initial intergrip distance of 2 cm were used. The exact width and the average thickness of the each samples were recorded. All testing was done while the membrane was still wet.

3. Results and Discussion

### 3.1. Effect of DVB Content Upon Skin Formation and Cross-sectional Morphology

Changes in microstructure with increasing cross-linking level are summarized in Figs. 3, 4 and 5. As the cross-linking level increases, the dense skin at the bottom (i.e. at the solution/glass interface) is more pronounced (Fig. 3). However, for the S1 membrane a very thin layer, which serves as a solute barrier, has not developed (Fig. 6). By comparison, the other membranes have a non-porous thin layer at the bottom (Figs. 5B, C and D).

Electron micrographs of the cross-section of membranes containing 20% DVB (S4 membrane) show undissolved PS remaining in the precipitation layer at the dense bottom. This is due to the relatively low solvent percentage associated with the corresponding initial high DVB concentration.
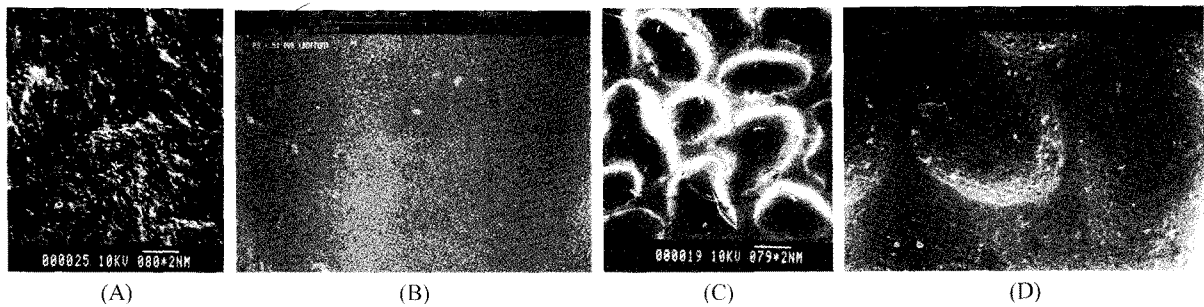
Macrovoids with open pores occur in the S1 mem-

(A)   (B)   (C)   (D)
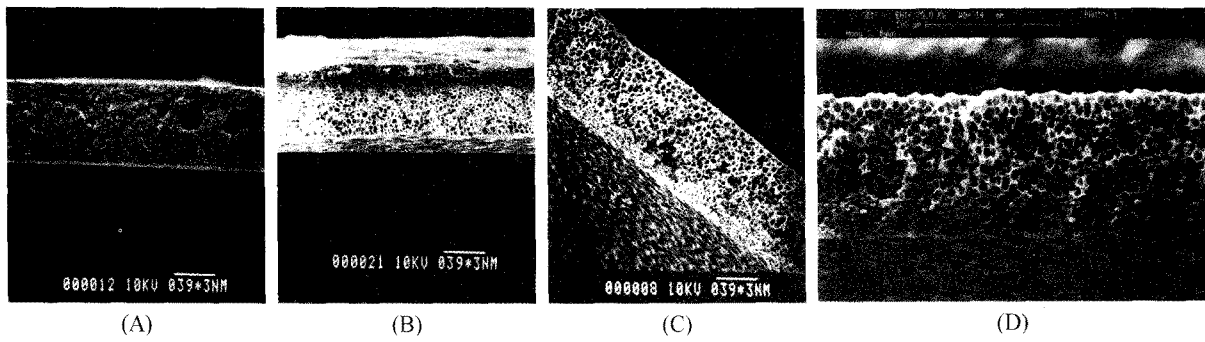
Fig. 3. Electron micrographs of the cross-section of cross-linked/asymmetric membranes: (A) S1, (B) S2, (C) S3 and (D) S4 (The scale bars correspond to 39 μm for A, B, C, and 100 μm for D. Magnification is 400X)

(A)   (B)   (C)   (D)
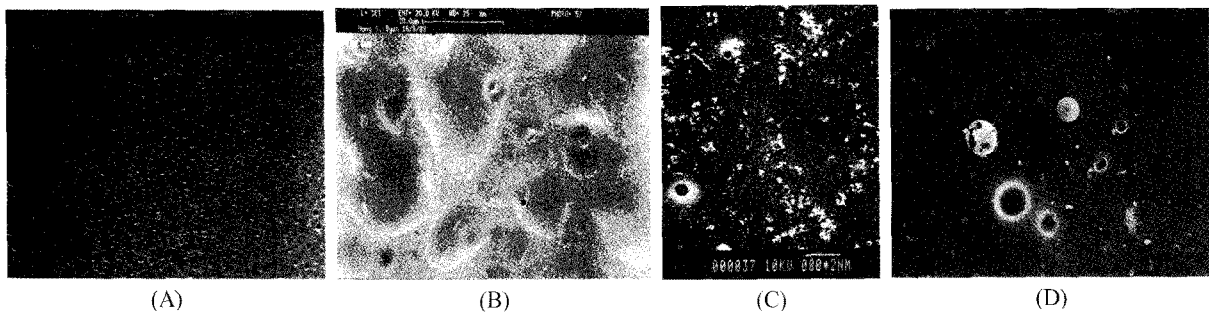
Fig. 4. Electron micrographs of the top surface of cross-linked/asymmetric membranes: (A) S1, (B) S2, (C) S3 and (D) S4 (The scale bars correspond to 20 μm for A, B, C, and 100 μm for D. Magnification is 2000X).


(A)   (B)   (C)   (D)

Fig. 5. Electron micrographs of the bottom surface of cross-linked/asymmetric membranes: (A) S1, (B) S2, (C) S3 and (D) S4 (The scale bars correspond to 20 μm for A, B, C, and 100 μm for D. Magnification is 2000X).

brane (Fig. 6). No well-formed skin exists either at the top (i.e. air/solution interface) or bottom (Figs. 6B and C) and uniform pores with macrovoids can be seen which are predicted to give high water flux and virtually no rejection. When casting solutions were prefiltered through a Du Pont 15~40 mm pore size disc microfilter to remove undissolved matter (including some high molecular weight polymer), membranes with a different structure were formed (Fig. 6E). Although in this case less macrovoids and bubbling occurred in

the liquid film during the casting process, a final membrane containing more finger type pores was obtained. The densely pored underlying structure is qualitatively similar to the unfiltered membrane. At high DVB levels prefiltration had little effect on membrane structures.

Figs. 4 and 5 show changes in the top and bottom surfaces with various DVB contents. The S1 membrane shows a highly porous structure at the top surface (Fig. 4), while the others show almost non-porous structures.

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| (A) | (B) | (C) | (D) | (E) |
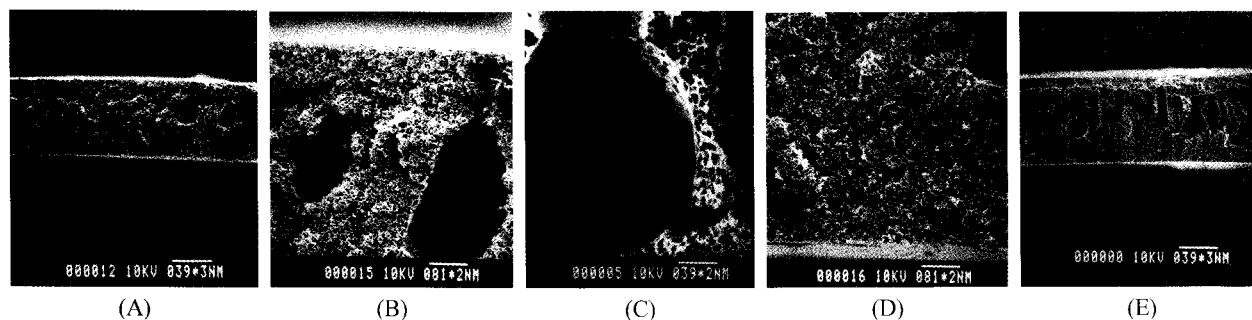
Fig. 6. Electron micrographs of the S1 membrane: (A) Cross-section, (B) Magnification of top side in the cross-section shows no dense skin. (C) Macrovoids with open pores are observed. (D) Magnification of bottom side in the cross-section shows no dense layer. (E) Cross-section of the S1 membrane cast from the unifiltered solution (The scale bars correspond to 39 μm for A and E, 8.1 μm for B and D, and 3.9 μm for C. Magnifications are 400X for A and E, 2000X for B and D, and 4000X for C.).

A Top Surface	B Top surface
A Cross-section	B Cross-section
A Bottom Surface	B Bottom Surface
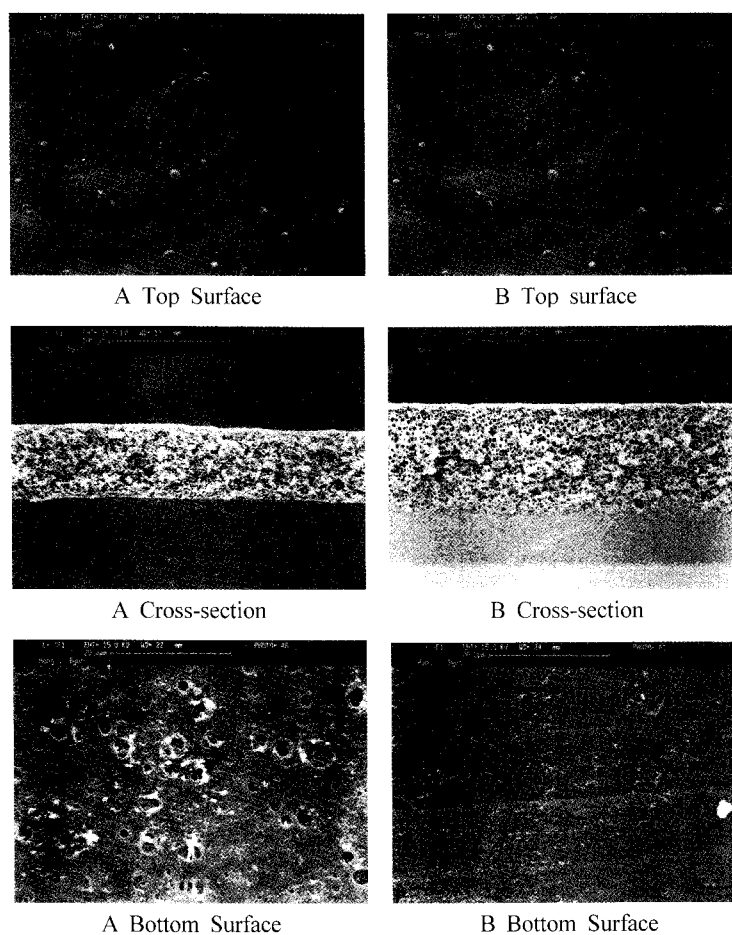
Fig. 7. Structural changes with polymer concentration in the S5 and S6 membrane; (A) 10% PS in the casting solution, (B) 40% PS in the casting solution (The scale bars correspond to 20 μm for the top and bottom surfaces, and 100 μm for the cross-section structure. Magnifications are 2000X for the top and bottom surfaces and 400X for the cross-section structure).

The effects of the concentration of PS on the final membrane structure are shown in Fig. 7. These mem- branes have similar compositions to the S1 membrane except for the PS concentration. When the PS contents

Table 2. Mechanical Properties of Cross-linked Asymmetric Membranes with Various Cross-linking Levels

DVB content in casting solution (membrane code)	Average tensile strength at break (MPa)	Average elongation at break (%)	Average elastic modulus (MPa)
2% (S1)	2.2	1.1	197
5% (S2)	2.9	1.7	243
10% (S3)	3.9	2.4	250
20% (S4)	4.4	2.1	326

Table 3. Effect of Rubber Content on Mechanical Properties of Cross-linked Membranes

Difference in casting solution (membrane code)	Average tensile strength at break (MPa)	Average elongation at break (%)	Average elastic modulus (MPa)
Membrane without rubber (S3)	3.9	2.4	251
Membrane with SBS (S5)	3.3	1.7	278
Membrane with PBD (S6)	2.5	1.6	234

were high enough (40%) to phase separate in the coagulation process, a non-porous skin was formed at the top surface and a very thick dense skin was formed at the bottom surface (Fig. 7B). On the other hand, if the PS content was not sufficient in the castin gsolution (10%), no skin was formed on either side (Fig. 7A)

3.2. Structural Changes with Different Casting Compositions

Fig. 7 shows the effect of casting composition on the membrane structure. S5 and S3 membranes were cast with the same DVB concentration as the S3 membrane except for the PS and rubber contents. These membranes have very uniform pore structures over the entire cross-section (Figs. 7A and B). However, the S5 membrane has some similarities with the S3 membrane, which is attributable to the contribution of 25% PS contents in the SB rubber itself, which increase the overall effective PS content in the casting solution.

3.3. Mechanical Properties of Cross-linked Membranes

The mechanical properties of cross-linked membranes are summarized in Tables 2 and 3. However, this experiment should be recognized as a screening test to determine if any dramatic changes occur. Tensile strength, elongations at break and elastic modulus increased slightly with increase in DVB content in the casting solution as expected. The effects of rubber and PS contents on the mechanical strength are shown in Table 3. the tensile strength of the S5 membrane was higher than that of the S6 membrane. This may be due

to the higher compatibility of the system PS-co-DVB/SB than the PS-co-DVB/PBD system, which correlates well with the results from the electron microscopy. Decreased elongation was obtained in the case of membranes containing rubber, indicating that the rubber content was insufficient to dramatically alter mechanical properties.

4. Conclusions

PS-co-DVB asymmetric membranes were successfully prepared, which their structure and mechanical properties were able to be controlled. It was revealed that the concentration of polymer in the casting solution played an important roll on the determination of the skin formation.

If the membrane had the lowest initial polymer concentration, the gelation did not occur during the coagulation process, resulting in no thin and dense "skin" at the top while the others indicated that the initial polymer concentrations were sufficient to from the non-porous "skin". This trend could be clearly seen from the electron micrographs of the top surfaces in Fig. 7. When the polymer concentration was high enough to initiate gelation in the coagulation beth, a thin and dense gel layer could be obtained. However, a thick dense layer and a non-porous skin at the bottom side was obtained with higher polymer concentration. This indicates that if the initial polymer concentration is high in the casting solution, a polymer adsorption at

the bottom associated with a phase separation at the top occurs, leading to the double "skinned" membrane.

The great influence of DVB content in the formation of skin at the bottom was also found. As cross-linking degree increases, a tighter network at the bottom is produced due to the severe cross-linking of polymer with monomer, resulting in a difficulty of penetration of non-solvent. This leads to a decrease in pore size at the bottom. However, if the DVB content is much higher (20%), a tight network is formed over the entire cross-section with predominantly closed pores in the bulk and a thick dense skin at the bottom.

When the PS-co-DVB membrane consists of SB rubber or liquid PBD, the structures formed show that the PS content in the PS/DVB system plays an important role in determining the porous sublayer structure. The cross-section of the S5 membrane has a rather similar structure to the S3 membrane, possibly due to the contribution of 25% PS content in the SB rubber itself, which increases the overall effective PS content in the casting solution. This trend was previously demonstrated in Fig. 7. Another likely contribution is the higher cross-linking predicted for the PS-co-DVB/SB system due to the high compatibility of the system. As a consequence, a slight polymer adsorption at the bottom was obtained. This structure correlates well with the result obtained from the mechanical properties. It was found that SB rubber could cause more cross-linking than PBD. Changes in structure with cross-linking degree correlate well with changes in the mechanical properties.

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