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SCIENTIFIC PAPER

UDC 678.028:678.7:66

DOI 10.2298/CICEQ110315017M

CURING AND MECHANICAL PROPERTIES OF CHLOROSULPHONATED POLYETHYLENE RUBBER BLENDS

In this paper, the curing and mechanical properties of two series of prepared blends, i.e., chlorosulphonated polyethylene (CSM)/isobutylene-co-isoprene (IIR) rubber blends and chlorosulphonated polyethylene (CSM)/chlorinated isobutylene-co-isoprene (CIIR) rubber blends were carried out. Blends were prepared using a two-roll mill at a temperature of 40-50 °C. The curing was assessed using a Monsanto oscillating disc rheometer R-100. The process of vulcanization accelerated sulfur of pure rubbers and their blends was carried out in an electrically heated laboratory hydraulic press under a pressure of about 4 MPa and 160 °C. The stress-strain experiments were performed using a tensile tester machine (Zwick 1425). Results indicate that the scorch time, t_{s2} , and optimum cure time, t_{c90} , increase with increasing CSM content in both blends. The value of modulus at 100 and 300% elongation and tensile strength increases with increasing CSM content, whereas elongation at break shows a decreasing trend. The enhancement in mechanical properties was supported by data of crosslink density in these samples obtained from swelling measurement and scanning electron microscopy studies of the rubber blends fractured surfaces.

Key words: CSM/CIIR rubber blend; CSM/IIR rubber blend; curing properties; mechanical properties; cross-link density; scanning electron microscopy.

Blends of rubbers are of technological and commercial importance, since they allow the user to access properties of the final blended and vulcanized rubber that are not accessible from a single, commercially available rubber alone. These potentially improved properties include chemical, physical, and processing benefits. In reality, all blends show compositionally correlated changes in all of these properties compared to the blend components. The technology of rubber blends is largely focused on the choice of individual rubbers and the creation of the blends to achieve a set of final properties [1]. Miscible blends of rubbers that consist of a single rubber phase with microscopically uniform cross-linking and distribution of reinforcing agents reflect a compositionally weighted average of the microscopic properties of the constituents. Miscible blends are commonly used though they have been very rarely recognized. Analysis of such blends, particularly after vulcanization, is diffi-

cult. The current analytical techniques are only slightly more capable than the classical techniques of selective precipitation of the components of an unvulcanized rubber blend from solution [2]. Immiscible blends show additional, more complex changes due to a microscopically inhomogeneous phase structure of the two component rubbers. The two separate phases typically have differences in the retention of the fillers and plasticizers as well as vulcanization in the presence of the curative. Changing the properties of rubbers by uneven distribution of fillers and vulcanization is, however, the more common use of blends of immiscible rubbers [3]. Many reviews [4-6] are focused on immiscible blends of rubbers. Isobutylene-based rubbers include butyl rubber and halogenated butyl rubber, due to their impermeability and resistance to heat and oxidation, these polymers find application in tire innerliners, innertubes, curing bladders and envelopes, and other specialty applications where air retention and resistance to heat and oxidation are desired [7]. Chlorosulfonated polyethylene (CSM) is an important rubber which has been frequently used in many applications such as sheeting

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Paper received: 15 March, 2011

Paper revised: 20 April, 2011

Paper accepted: 28 April, 2011

cable and geomembrane due to its outstanding resistance to deterioration by heat, oils, ozone and oxidation [8]. The blending together of isobutylene-based rubbers (IIR) with chlorosulphonated polyethylene (CSM) is intended to produce a vulcanizate with the best properties from each component, *i.e.*, CSM's impermeability and IIR and CIIR's good strength properties and resistance to oil [9]. Chlorobutyl (CIIR) and bromobutyl (BIIR) rubbers are manufactured similarly to butyl rubber, but with an added subsequent halogenation step. Due to the nearly equivalent reactivity ratios of the monomers and low concentration of isoprene, the isoprenyl units in these polymers are randomly distributed along the polymer chain. Commercially, chlorobutyl rubber (CIIR) and bromobutyl rubber (BIIR) are the most important derivatives of butyl rubber. Their predominant application is in tire innerliners with the performance of the modern radial tire being impacted by the amount of halobutyl rubber used in the innerliner compound. Typical performance requirements of the tire innerliner are: air retention, adhesion to tire carcass compound, resistance to fatigue and cracking, heat resistance, high tensile and tear strength [10]. In this study, two series of prepared blends, *i.e.*, chlorosulphonated polyethylene (CSM)/isobutylene-co-isoprene (IIR) rubber blends and chlorosulphonated polyethylene (CSM)/chlorinated isobutylene-co-isoprene (CIIR) rubber blends were carried out. The rheometric characteristics of these materials, such as scorch safety and cure rate were analyzed. The mechanical properties were also investigated as a function of blend ratio. The cross-link density was obtained from swelling measurements and the morphology of the rubber blends fractured surfaces was investigated using scanning electron microscopy studies.

EXPERIMENTAL

Materials

Two different types of rubbers were used IIR and CIIR and blended with CSM at different ratios. IIR (Butyl 068), Mooney viscosity 51 (ML1+8 at 125 °C) with isoprene content of 1.15 mol% and CIIR (Chlorobutyl 1066), Mooney viscosity 38 (ML1+8 at 125 °C) with isoprene content of 1.95 mol% and halogen con-

tent of 1.26 mol% were supplied by ExxonMobil, England. Their respective technical specifications are shown in Table 1.

Sulfur, MBT and TMTD were used as a vulcanizing agent and accelerator, respectively, throughout this study. Commercial grade rubber chemicals such as zinc oxide and stearic acid were also used. For each of the two types of rubbers, IIR and CIIR with various ratios of CSM the cure systems were incorporated. The details of the blend ratios are shown in Table 2. In each cure system, blends in gum vulcanizates were prepared with containing 5.0 phr (parts per hundred parts of rubber) zinc oxide, 2.0 phr stearic acid, 0.5 phr MBTS, 2 phr TMTD and 2 phr sulfur.

Compounding

The compound formulation is given in Table 2.

Table 2. Blend formulations (phr) of IIR and CIIR with CSM (cure system: 5.0 phr zinc oxide, 2.0 phr stearic acid, 0.5 phr MBTS, 2 phr TMTD, and 2 phr sulfur)

CSM	IIR/CIIR
100	0
80	20
60	40
40	60
20	80
0	100

Testing

The cure characteristics were assessed by a Monsanto oscillating disc rheometer R-100. The various rubber blends were compression molded into 2 mm-thick test specimen sheets at 160 °C according to their respective optimum cure times. Dumbbell-shaped specimens were cut from the molded sheets with a width of 6.3 mm±0.1 mm. Tensile testing procedure was carried out in accordance with ASTM 412-98a [11] using an Instron universal testing machine (Zwick 1425) operating with a crosshead speed of 50 cm/min.

Swelling properties

The resistance of the vulcanizates to toluene was determined by using the method described in ASTM-D3010. Three different shapes of the cured

Table 1. Technical specification of isobutylene-co-isoprene (IIR), chlorinated isobutylene-co-isoprene (CIIR) and chlorosulphonated polyethylene (CSM) rubbers

Elastomer	Grade	Mooney viscosity (ML1+8 at 125 °C)	Isoprene (mol%)/ Sulphur content (mol%)	Halogen	Halogen mol%
Isobutylene-co-isoprene (IIR) rubber	Butyl 068	51	1.15	-	-
Chlorinated isobutylene-co-isoprene (CIIR) rubber	Chlorobutyl 1066	38	1.95	Cl	1.26
Chlorosulphonated polyethylene (CSM) rubber	Hypalon 40S	46	1.00	Cl	34.5

samples were cut from the 1 mm thickness mould and weighed and immersed in air tight containers of diesel, kerosine and toluene solvents at ambient temperature for 24 h. The samples were then removed from the bottles wiped dry with filter paper and weighed immediately. The change in weight of the sample was expressed as percentage swelling:

$$Q = 100(m_1 - m_0) / m_0 \quad (1)$$

where m_1 and m_2 are the initial and final weight of the swollen sample respectively. Crosslink density, ν , of the rubber blends composites can be estimated from swelling measurement, using the Flory-Rehner equation [12].

Scanning electron microscopy

The scanning electron microscopy images of the rubber blends fractured surfaces were taken by a JEOL JSM-5400 model of the microscope. The samples were sputter coated with gold for 3 min under high vacuum with image magnifications of 2000 \times .

RESULTS AND DISCUSSION

Curing characteristics

Figures 1 and 2 show the effect of CSM content on the scorch t_{s2} and cure time, t_{c90} , of the CSM/IIR and CSM/CIIR rubber blends. It can be seen that the t_{s2} and t_{c90} of these blends increase with increasing CSM content. CIIR and CSM are polar rubber. As the content of CSM in the blends is increased, the curative agent, *i.e.*, sulphur, becomes more soluble in CSM and CIIR compared to IIR. Consequently the curing rate of the blend increases with increasing content of CSM [12-14] reported that for blends of two rubbers with similar polarity, distribution of crosslinks can be equal through phases.

It can be seen also in Figures 1 and 2 that at a similar CSM content, t_{s2} and t_{c90} of CSM/CIIR blend is shorter than CSM/IIR blend. The effect of CSM content on the maximum torque (M_h) is shown in Figure 3. It can be seen that the M_h increases with increasing CSM content in the CSM/CIIR blend. Figure 3 also shows that above about 40 phr of CSM, M_h of CSM/CIIR blends has higher values than CSM/IIR blend as a result of the miscibility presence between CSM and CIIR rubber. The relationship between the torque difference, $\Delta M = M_h - M_l$ (max. torque - min. torque) and content of CSM is shown in Figure 4. It is known that the torque difference indirectly relates to the cross-link density of the blends [15]. This figure clearly shows that CSM/CIIR blend is a more compatible blend than CSM/IIR blend. The decreasing torque differen-

ce for CSM/IIR indicates that a distribution of cross-link occurred which results in an over-crosslinked phase and a poorly crosslinked one.

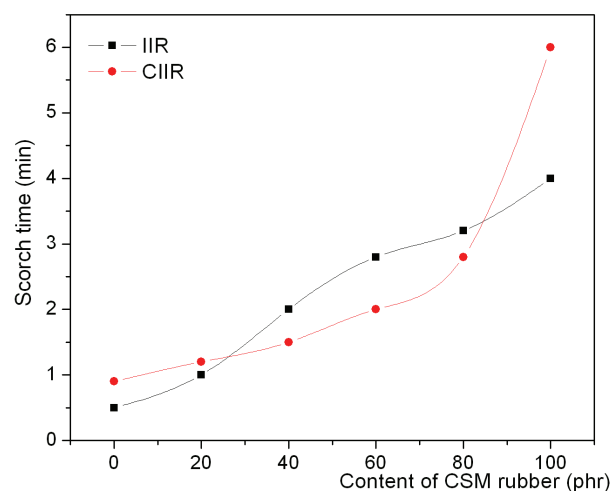


Figure 1. Variation of scorch time t_{s2} with CSM content at 160 °C for CSM/IIR and CSM/CIIR blends.

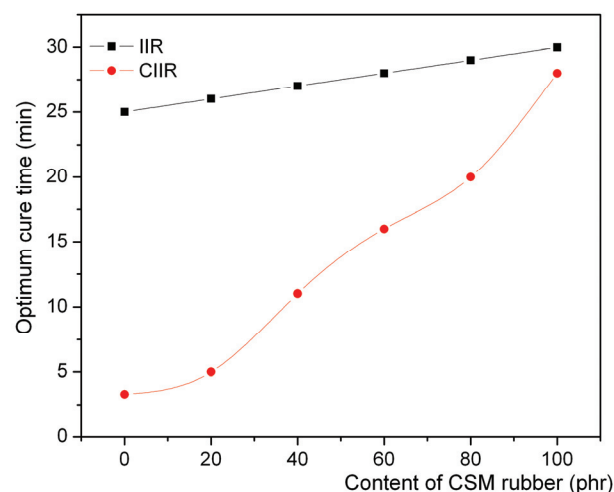


Figure 2. Variation of cure time t_{c90} with CSM content at 160 °C for CSM/IIR and CSM/CIIR blends.

Again at a similar CSM content, CSM/CIIR blend exhibits higher $M_h - M_l$ than CSM/IIR blend. Choi [16] reported that with normal sulphur vulcanizing systems, the efficiency of CIIR vulcanization seemed to be improved. The isolated double bonds in CIIR inhibit the formation of intramolecular sulphide links thus resulting in the increase of the crosslinking rate.

Mechanical properties

Figure 5 shows the variation of M100 with CSM content in the two CSM/IIR and CSM/CIIR rubber blends. It is obvious that as the percent of CSM increases, M100 also increases correspondingly. This

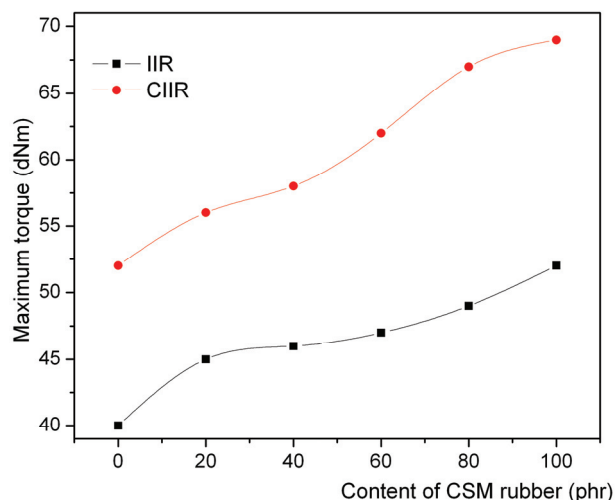


Figure 3. Maximum torque, M_h , versus CSM content at 160 °C for CSM/IIR and CSM/CIIR blends.

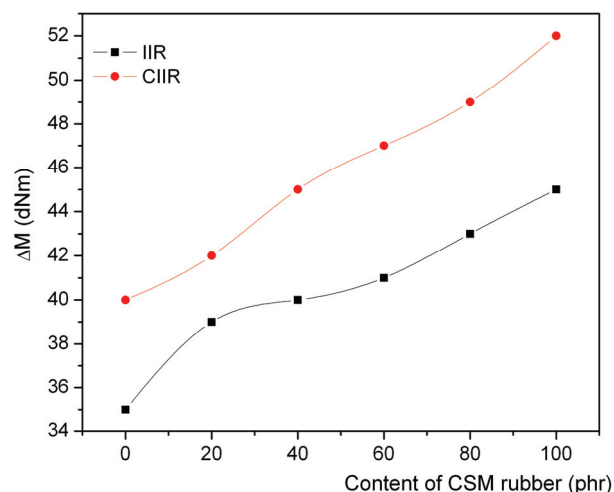


Figure 4. Torque difference ($M_h - M$) versus CSM content at 160 °C for CSM/IIR and CSM/CIIR blends.

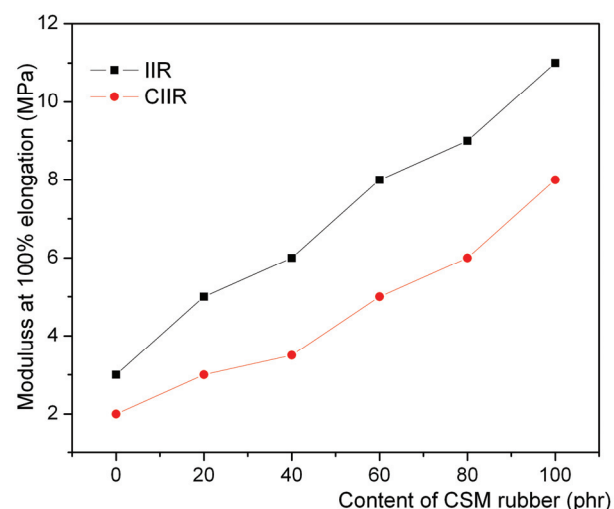


Figure 5. Variation of M_{100} with CSM content in the blends.

means that the incorporation of CSM in the blend would enhance cross-linking as M_{100} is a measure of degree of cross-linking. CSM/CIIR blend gives a higher M_{100} value than the CSM/IIR blends. This observation may be attributed to greater enhancement effect of CSM on CIIR. In fact, the crosslinking density is increase for both blends. As in the case of CSM/IIR blend, the lower M_{100} is attributed to the non-enhancement effect of CSM which is a polar polymer compared to IIR, a non-polar rubber. Thus, the CSM/IIR blend has a lower crosslinking density than CSM/CIIR blends.

The variation of M_{300} with CSM content is presented in Figure 6. In this case, CSM/IIR blend consistently shows a higher M_{300} than CIIR blends.

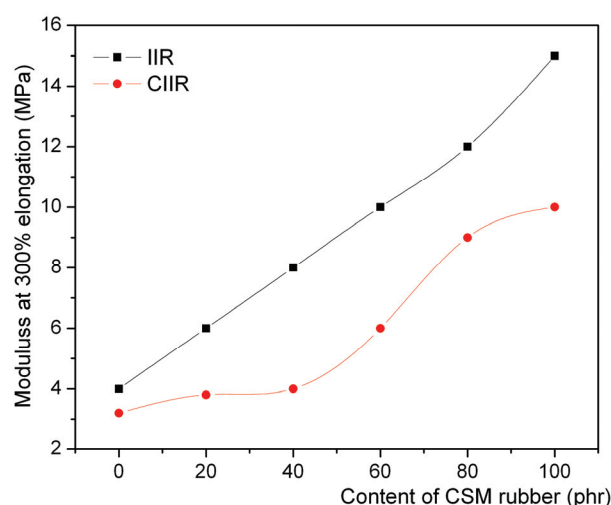


Figure 6. Variation of M_{300} with CSM content in the blends.

The increase of M_{300} values indicates that CSM reinforces IIR and CIIR blends: the degree of reinforcement is greatest in IIR, followed by CIIR as the degree of crystallization decreases with increasing % of halogenated. Figure 7 shows the dependence of tensile strength of the two rubber blends on CSM content. Again, IIR blend consistently indicates a higher tensile strength than the CIIR blend as observed for M_{300} . However, in this case, tensile strength decreases gradually with increasing CSM content for all the blends studied. This observation is associated with the decreasing effect of strain-induced crystallization as CSM content is increased. As discussed earlier in M_{300} , IIR exhibits the greatest strain-induced crystallization, followed by CIIR. This sequence of decreasing crystallization is reflected by the decreasing value of tensile strength for the respective single component rubbers [17]. In the case of CSM, it has the lower tensile strength due to the non-crystallizable nature of the rubber. Figure 7 also shows that

for CSM content greater than 60 phr, greater drop in tensile strength for the blends is observed. This finding may be ascribed to the dominant effect of CSM at higher loading of CSM.

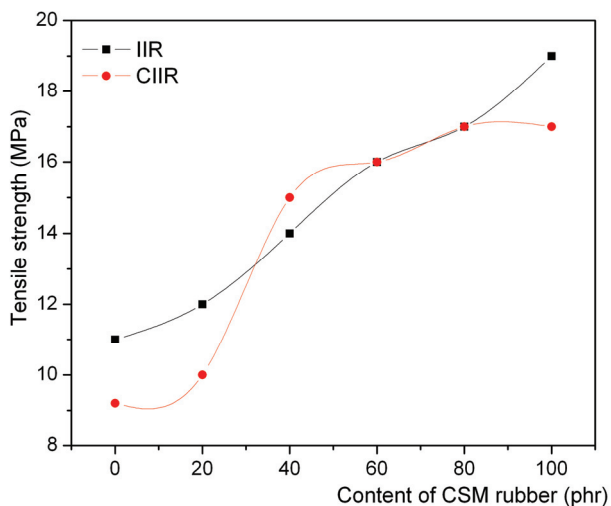


Figure 7. Variation of tensile strength with CSM content in the blends.

The effect of CSM on elongation at break for CSM/IIR and CSM/CIIR rubber blends is shown in Figure 8. The effect, in fact, is very similar to that of tensile strength, *i.e.*, elongation at break decreases gradually with increasing CSM content. Owing to the higher strength of IIR, its blend gives a much higher elongation at break compared to CIIR blend. For the single component CSM, its elongation at break is the lowest among the rubbers studied due to the non-crystallizable property of CSM.

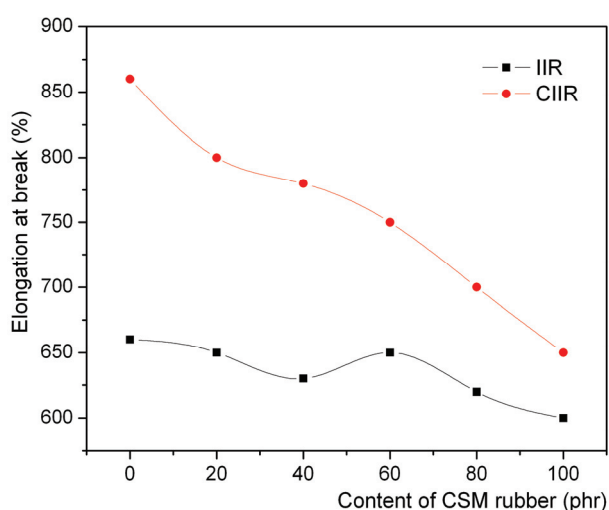


Figure 8. Variation of elongation at break with CSM content in the blends.

Swelling properties

Calculation of cross-link density from swelling behavior as one of the most important structural parameters characterizing a cross-linked polymer is the average molecular weight between the cross-links (directly related to the crosslink density) we determined it from swelling. The cross-link density, ν , is defined as the number of elastically active network chains totally included in a perfect network, per unit volume and is given by:

$$\nu = \rho_p N_A / M_c \quad (2)$$

where M_c is the average molecular weight of the polymer between cross-links and N_A is the Avogadro number. In the case of rubber composites the network of cross-linked macromolecules is never perfect, but still this calculating procedure is common in literature as a relative measure of crosslink density in rubbers [17]. According to the theory of Flory and Rehner for a perfect network:

$$M_c \equiv -V_1 \rho_p \frac{(\Phi_p^{1/3} - \frac{\Phi_p}{2})}{\ln(1 - \Phi_p) + \Phi_p + \chi \Phi_p^2} \quad (3)$$

where V_1 is the molar volume of the solvent, ρ_p is the polymer density, Φ_p is the volume fraction of the polymer in swollen gel, and χ is the Flory-Huggins interaction parameter. Some calculated data for the “relative” cross-link density values, ν , obtained from the swelling measurements for rubber blends are given in Table 3. The cross-link density is found to slightly change with an increase in concentration of the CSM rubber in CSM/CIIR and CSM/IIR rubber blends. Higher cross-link density is obtained for CSM/CIIR rubber blends; this is because of the restriction of swelling due to the similar (polar) nature of rubbers and formation of new cross-links according to free sulphur and residues of curatives react with rubbers, which causes an increase in Φ_p and increases the cross-link density. Thus, the observed tensile strength variation can be exactly correlated with the variation of ν from swelling studies. In swelling studies of these samples, crosslinks are flexible to penetrate, but as the loading of CSM increases they restrict the swelling. The swelling ratio, $1/Q$ calculated using Eq. (1) is found to increase (Table 3).

Morphological study

On Figures 9a and 9b, the SEM photomicrograph of CSM/IIR and CSM/CIIR (60/40) rubber blends at 2000 \times magnification are shown. The micrograph of CSM/CIIR (Figure 9b) exhibits that the composite's surface is rough with many tear lines and branching.

Table 3. Data for the crosslink density (ν), reciprocal swelling ratio ($1/Q$), volume fraction of CSM/CIIR and CSM/IIR rubber blends in swollen gel (Φ_p), molecular weight between the crosslink (M_c), and Flory-Huggins parameter (χ) from swelling measurements

Sample	$\nu \times 10^2 / \text{mol dm}^{-3}$	Φ_p	$1/Q$	$M_c / \text{g mol}^{-1}$	χ
CSM/IIR/CIIR (100/0/0)	710	0.3200	0.4780	750	0.4221
CSM/IIR/CIIR (80/20/0)	795	0.3300	0.4760	762	0.4187
CSM/IIR/CIIR (60/40/0)	800	0.3321	0.4733	778	0.4080
CSM/IIR/CIIR (40/60/0)	810	0.3381	0.4720	780	0.4050
CSM/IIR/CIIR (20/80/0)	830	0.3397	0.4709	793	0.4010
CSM/IIR/CIIR (0/100/0)	832	0.3399	0.4700	790	0.4100
CSM/IIR/CIIR (80/0/20)	812	0.3312	0.4750	770	0.4200
CSM/IIR/CIIR (60/0/40)	824	0.3330	0.4720	791	0.4150
CSM/IIR/CIIR (40/0/60)	831	0.3393	0.4712	814	0.4110
CSM/IIR/CIIR (20/0/80)	847	0.3400	0.4700	831	0.41040
CSM/IIR/CIIR (0/0/100)	850	0.3411	0.4687	821	0.4190

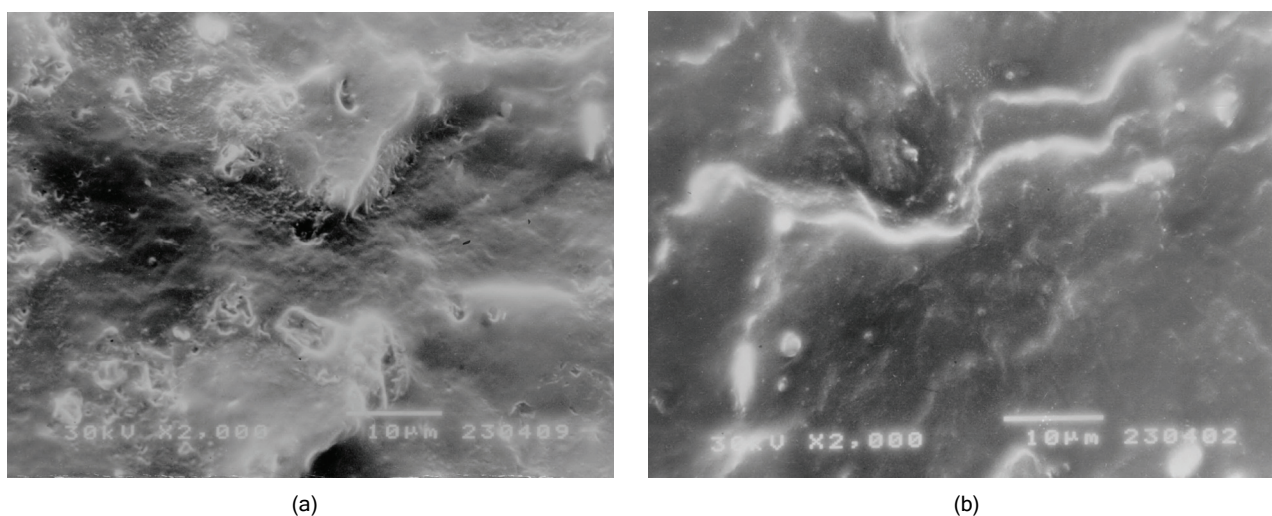


Figure 9. SEM micrograph of CSM/IIR (60/40) (a) and CSM/CIIR (60/40) rubber blends (b).

This type of failure indicates the higher tensile strength and a weak interaction between CSM and CIIR rubbers.

CONCLUSIONS

The incorporation of CSM in CSM/IIR, and CSM/CIIR blends increases the scorch, t_{s2} , and cure time, t_{c90} . At a similar CSM content, the CSM/CIIR blend exhibits shorter scorch t_{s2} and cure time t_{c90} than the CSM/IIR blend. The incorporation of CSM in the CSM/CIIR blend also increases the maximum torque (M_h) and torque difference ($M_h - M_l$). However, for the CSM/IIR blend the maximum torque and torque difference decrease with incorporation of CSM, an observation which is attributed to the maldistribution of cross-link between the two rubber phases. M100 and M300 increase with increasing CSM content in both blends. The former increase is attributed to the enhancing effect of CSM and the latter increase is associated with strain-induced crystallization of the res-

pective rubbers. Tensile strength and elongation at break of the blends decrease gradually with CSM content, an observation which is ascribed to the decreasing effect of strain-induced crystallization of IIR and CIIR as CSM content is increased in the respective blends. The cross-link density is found to slightly change with an increase in concentration of the CSM rubber in CSM/CIIR and CSM/IIR rubber blends. Higher cross-link density is obtained for CSM/CIIR rubber blends. The micrograph of CSM/CIIR exhibits that the composite's surface is rough with many tear lines and branching indicates the higher tensile strength and a weak interaction between CSM and CIIR rubbers.

Acknowledgement

Financial support for this study was granted by the Ministry of Science and Technological Development of the Republic of Serbia (Projects Nos. 45022 and 45020).

REFERENCES

- [1] G. Marković, S. Samaržija-Jovanović, V. Jovanović, M. Marinović-Cincović, J. Budinski-Simendić, *Chem. Ind. Chem. Eng. Q.* **15**(4) (2009) 291-298
- [2] A.M. Omran, A.M. Youssef, M.M. Ahmed, E.M. Abdel-Bary, *Kautch. Gummi Kunst.* **6** (2010) 197-202
- [3] S. Wu, *Polymer* **26**(12) (1985) 1855-1863
- [4] G. Marković, S. Samaržija-Jovanović, V. Jovanović, M. Marinović-Cincović, J. *Therm Anal. Calor.* **100** (2010) 881-888
- [5] H. Essawy, D. El-Nashar, *Polym. Test.* **23**(7) (2004) 803-807
- [6] G. Marković, B. Radovanović, M. Marinović-Cincović, J. Budinski-Simendić, *Kautch. Gummi Kunst.* **5** (2006) 251-255
- [7] A. Voet, *J. Polym. Sci.* **15** (1980) 327-373
- [8] P.J. Flory, *Ind. Eng. Chem.* **38**(4) (1946) 417-436
- [9] A. Roychoudhury, P.P. De, *J. Appl. Polym. Sci.* **63**(13) (1997) 1761-1768
- [10] L. Zhang, Y. Wang, Y. Wang, Y. Sui, D. Yu, *J. Appl. Polym. Sci.* **78**(11) (2000) 1873-1878
- [11] ASTM 412-98a
- [12] R. Ding, A.I. Leonov, *J. Appl. Polym. Sci.* **61**(3) (1966) 455-463
- [13] B.T. Poh, K.W. Wong, *J. Appl. Polym. Sci.* **69**(7) (1998) 1301-1305
- [14] R. de León, G. Morales, P. Acuña, F. Soriano, *Polym. Eng. Sci.* **50**(2) (2010) 373-383
- [15] S.S. Choi, *J. Appl. Polym. Sci.* **75**(11) (2000) 1378-1384
- [16] G. Marković, M. Marinović-Cincović, B. Radovanović, J. Budinski-Simendić, *Chem. Ind. Chem. Eng. Q.* **13**(4) (2007) 186-191
- [17] B. Radovanović, G. Marković, A. Radovanović, *Polym. Compos.* **29** (2008) 692-697.

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NAUČNI RAD

REOLOŠKA I MEHANIČKA SVOJSTVA BLENDI HLOROSULFONOVANOG POLIETILENSKOG KAUČUKA

U ovom radu ispitana su reološka i mehanička svojstva dve serije blendi kaučuka hlorsulfonovanog polietilenskog (CSM) i izobutilen izoprenskog kaučuka (IIR) i hlorsulfonovanog polietilenskog (CSM) i hloriganog izobutilen izoprenskog kaučuka (CIIR). Blende su pripremljene na laboratorijskom dvovaljku na temperaturi od 40-50 °C. Reološka merenja su izvršena pomoću oscilujućeg disk reometra (Monsanto R-100). Vulkanizacija sumporno umreženih pojedinačnih kaučuka i njihovih blendi rađena je u hidrauličnoj presi na 4 MPa i 160 °C. Eksperimenti napon-istezanje rađeni su na mašini Zwick 1425. Rezultati pokazuju da se početak umrežavanja t_{s2} , optimalno vreme umreženja t_{c90} , modula 100 i 300%, prekidne jačine i tvrdoće uvećavaju, dok se vrednosti prekidnog izduženja i procenta bubrenja smanjuju za oba sistema blendi sa povećanjem sadržaja CSM kaučuka. Poboljšanje mehaničkih svojstava upotpunjeno je dobijenim vrednostima za gustinu umreženja metodom bubrenja, kao i slikama preloma površina blendi skenirajućom elektronskom mikroskopijom.

Ključne reči: blenda kaučuka CSM/CIIR; reološka svojstva; mehanička svojstva; gustina umreženja; skenirajuća elektronska mikroskopija.