

Thermostability and surface morphology of nano- and micro-filled NBR/CSM and CR/CSM rubber blends

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Abstract: Acrylonitrile-butadiene rubber (NBR), polychloroprene rubber (CR), chlorosulphonated polyethylene rubber (CSM) and their blends were cross-linked with sulphur, ethylene-thiourea, magnesium oxide or their combination. The effect of nano- and micro- particle sized of 35 pphr SiO₂ on the thermostability and surface morphology of all the crosslinked systems was investigated. Identification of the structure of nano- and micro- particle sized SiO₂ filled NBR/CSM and CR/CSM crosslinked systems was carried out by Fourier transform infrared spectroscopy (FTIR) with an attenuated total reflectance (ATR) extension. The thermal stability of the nano- and micro- particle sized SiO₂ filled NBR/CSM and CR/CSM crosslinked systems were carried out by thermogravimetric analysis (TGA). The glass transition temperature (T_g) of the samples was determined by differential scanning calorimetry (DSC). The morphology of the fracture surface of the crosslinked systems was carried out by scanning electron microscope (SEM). The results show when filled with nano-particle sized of SiO₂ NBR/CSM and CR/CSM polymer matrix have a strong peak from SiO–C at 1079 cm⁻¹. This suggests the an interaction between the SiO₂, which should lead to an increased thermal stability, higher values of T_g , better dispersion the nano-SiO₂ and more polish, without cracks than micro-filled NBR/CSM and CR/CSM crosslinked systems.

Keywords: IR spectral analysis, thermal stability, glass transition temperature, surface morphology, nano- and micro- particle size of SiO₂ filled NBR/CSM and CR/CSM crosslinked systems.

INTRODUCTION

About 75 % of all crosslinked rubber systems are used as blends rather than alone. Blends of two or more polymers are often used, because thereby optimal properties for specific applications can be obtained.^{1,2}

Hoffman and coworkers² investigated crosslinked NBR/EPDM rubber systems and concluded that these systems have a high ozone resistance. R. S. Popović and M. Plavšić¹

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investigated a crosslinked system based on acrylonitrile-butadiene rubber (NBR) and silicone rubber (MQ). R. E. Fuleir and K. S. Macturk showed that a crosslinked NR/CSM rubber system in a mass ratio of 50:50 has good weather resistance, color stability and high extension values.³ The effect of filler on the properties of a composite, as well as on the interaction of the fillers with the matrix was studied.^{6,7}

This paper presents a crosslinked systems based on acrylonitrile-butadiene rubber (NBR), polychloroprene rubber (CR), chlorosulphonated polyethylene rubber (CSM), NBR/CSM and CR/CSM rubber blends filled with 35 pphr SiO₂. For the curing of the elastomers and the systems of two elastomers, the following crosslinking systems were used: sulphur, ethylene-thiourea, magnesium oxide and their combinations. Identification of the structure the nano- and micro- particle sized SiO₂ filled NBR/CSM and CR/CSM crosslinked systems was carried out by Fourier transform infrared spectroscopy (FTIR) with a attenuated total reflectance (ATR) extension. The thermal stability of the nano- and micro- particle sized SiO₂ filled NBR/CSM and CR/CSM crosslinked systems was carried out by thermogravimetric analysis (TGA). The glass transition temperature (T_g) of the samples was determined by differential scanning calorimetry (DCS). The morphology of the fracture surface of the crosslinked systems was investigated by scanning electron microscope (SEM).

EXPERIMENTAL

The compounds (Table I) were prepared using a laboratory mixing roll mill of dimensions 400×150 mm at a speed ratio of the rollers $n_1/n_2 = 28/22$, at a roller temperature of 40–50 °C.⁸

The time of the preparation of the blends was *ca.* 20 min. Curing was done at 160 °C up to the optimum cure time (t_{c90}) which was determined from the rheograph which was obtained using a Monsanto R-100 model. The formulations of the samples used in this study are listed in Table I.

TABLE I. Formulation of the crosslinked systems based on acrylonitrile butadiene rubber (NBR), polychloroprene rubber (CR), chlorosulphonated polyethylene rubber (CSM), and nano- and micro-particle sized SiO₂ filled NBR/CSM and CR/CSM crosslinked systems

Compounds/pphr ^a	1	2	3	4	5	6	7	8	9
NBR ^b	100	–	50	50	50	–	–	–	–
CSM ^c	–	100	50	50	50	–	50	50	50
CR ^d	–	–	–	–	–	100	50	50	50
ZnO	5	–	2.5	2.5	2.5	5	2.5	2.5	2.5
Stearic acid	2	2	2	2	2	2	2	2	2
SiO ₂ ^e	–	–	–	35	–	–	–	35	–
SiO ₂ ^f	–	–	–	–	35	–	–	–	35
Naphthenic oil ^g	–	–	–	11	11	10	10	10	10
MgO ^h	–	4	2	2	2	–	2	2	2
ETU ⁱ	–	–	–	–	–	1	0.5	0.5	0.5

TABLE I. Continued

Compounds/pphr ^a	1	2	3	4	5	6	7	8	9
TMTD ^j	2.5	2	2.5	2.5	2.5	–	1.0	1.0	1.0
CZ ^k	2	–	1	1	1	–	–	–	–
S	0.5	1	0.75	0.75	0.75	–	0.5	0.5	0.5
Diethylene glykol	–	–	–	1.1	1.1	–	–	1.1	1.1

^aPart per hundred parts of rubber, ^bButadiene-acrylonitrile copolymer rubber–EUROPREN N3345, ^cChlorosulphonated polyethylene rubber – HYPALON 40S, ^dPolychloroprene rubber – BAYPREN 110, ^eWhite filler (15 nm) – ULTRASIL VN 3, ^fWhite filler (28 μm) – CELITE 281, ^gNaphthenic oil – TEPHIL NAPHTHENE P. O. 100, ^hMagnesium oxide – ANSCOR P, ⁱEthylene thiourea – ETU, ^jVery fast accelerator-tetramethylthiuram disulfide (TMTD), ^kLow fast accelerator – *N*-cyklohecsil-2-benzothiazol sulfenamide (VULKACIT CZ)

Infrared spectroscopy. Infrared (FTIR) spectroscopy with a ATR extension were performed using by BOMEM Hartmann & Braun MB series instrument. The samples of dimensions 50×20×2 mm were put on the ATR attachment.

Thermogravimetric measurements. Thermogravimetric (TG) measurements were performed using a Perkin Elmer TGS-2 instrument. The CR/CSM samples (mass about 5 mg) were heated from 30 to 700 °C at a heating rate of 10 °C min⁻¹ in oxygen and air using a gas flow rate of 30 ml min⁻¹.

Differential scanning calorimetry. The glass transition temperature (T_g) of the samples were determined in the temperature range –100 to +100 °C using a DuPont Differential Scanning Calorimeter.

Scanning electron microscopy studies. Examination of the fracture surface was carried out using a scanning electron microscope (SEM) model JEOL JSM 5300. The aim was to obtain some information on the mode of the fracture the condition of the matrix and filler surfaces and dispersion. The fracture ends in a nitrogen atmosphere and sputters coated with a thin layer of gold.

RESULTS AND DISCUSSION

The analytical data for nano- and micro-SiO₂ are shown in Table II.

TABLE II. Analytical data for the white fillers

	SiO ₂	SiO ₂
BET (N ₂)/m ² /g ⁻¹	160–200	–
DBP Absorption/(cm ³ /100 g)	220	130
pH	6.7	10
Particle size	15 nm	28 μm

IR spectral analysis

The FTIR spectra of the unfilled and nano- and micro-particle sized SiO₂ filled NBR/CSM and CR/CSM crosslinked systems are shown in Fig. 1.

In the spectra of pure CSM and NBR, the peak position of –SO₂Cl is at 1292 cm⁻¹, of S–Cl at 1192 cm⁻¹ and of C–Cl at 816 cm⁻¹ and at 975 cm⁻¹. In the spectrum of the 50:50 blend there is definite shift of the –SO₂Cl peak to 1300 cm⁻¹ and 1208 cm⁻¹ and of the

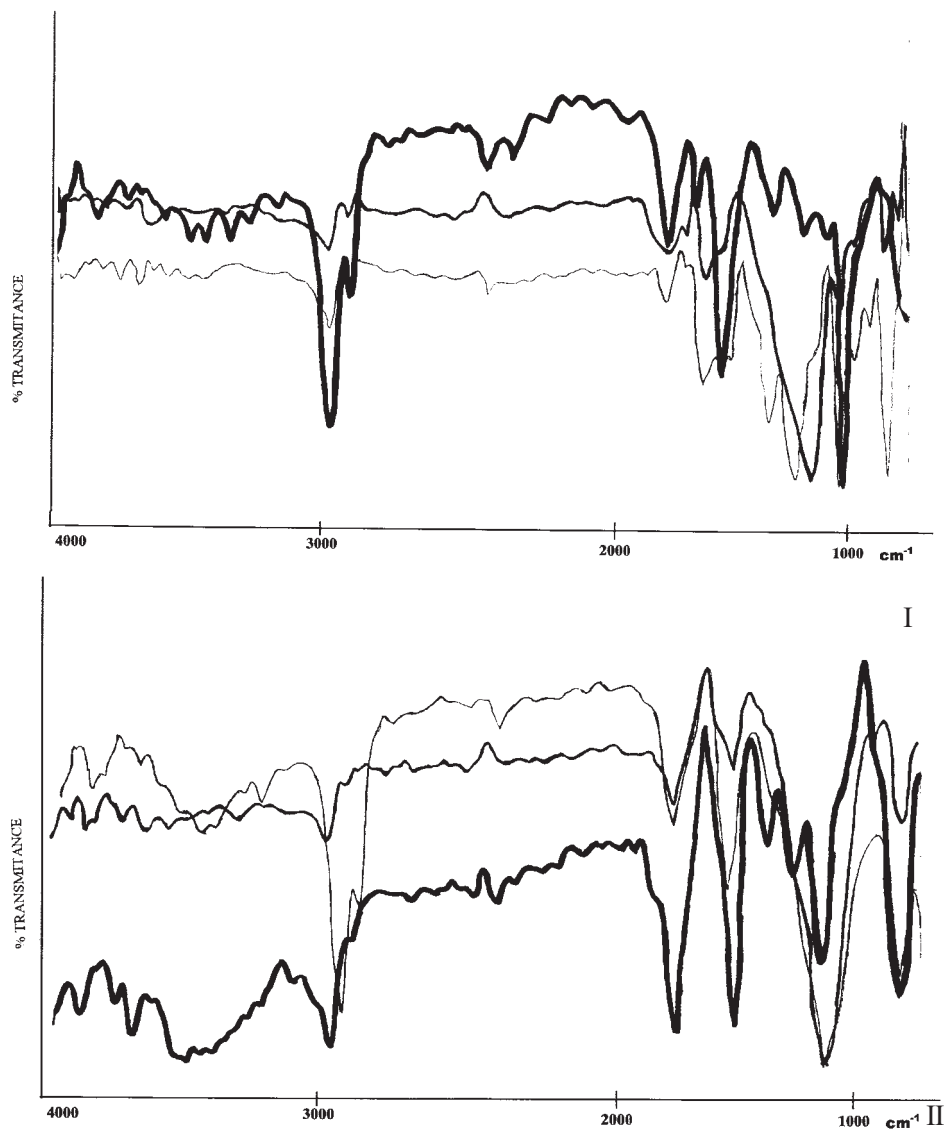


Fig. 1. FTIR spectra with ATR attachment of NBR/CSM (I) and CR/CSM (II) rubber blends: (—) – unfilled; (---) nano-SiO₂ filled; (· · ·) micro-SiO₂ filled.

–C–Cl peak to 808 cm⁻¹, but the other is not ad shift which suggests interactions.⁶ At elevated temperature radicals may be formed at the tertiary carbon atoms of the polymers. The absence of peaks of S–Cl in CR/CSM blends suggests the presence of R–SO₂–R groups. Reaction NBR/CSM polymer matrix with 35 pphr SiO₂ (15 nm), and the strong peak from SiO–C at 1079 cm⁻¹ in the spectra of the filled samples suggests interaction of the polymers matrix with the SiO₂.

Thermal stability

The thermal stability analysis was based on the temperature for certain weight losses, namely 10 and 30 %, and the rate of weight loss change as a function of temperature (first derivative of the dynamic TG curve) *i.e.*, the initial and overall shapes.⁸

The first corresponds to partial degradation of the sample and the second is the result of complete thermal decomposition. The samples could be characterized by the position of the decomposition peaks and their size, the difference being the result of the different influence of their structure and the differences in the degradation processes. The data for the 10 and 30 % weight loss temperatures are given in Table III.

TABLE III. Glass transition temperatures (T_g) for 10 and 30 % weight loss and other characteristic temperatures of unfilled and nano- and micro-particle sized SiO_2 filled NBR/CSM and CR/CSM crosslinked systems

Compounds	$T_{\max}/^{\circ}\text{C}$	$T_{10\%}/^{\circ}\text{C}$	$T_{30\%}/^{\circ}\text{C}$	$T_{\text{end}}/^{\circ}\text{C}$	$m_{\text{rest}}/\%$	$T_g/^{\circ}\text{C}$
NBR	434	403	427	707	3.37	-22
CSM	348	319	354	655	25.4	-37
NBR:CSM (50:50)	449	312	429	472	3.8	-20
NBR:CSM+ SiO_2 (15 nm)	452	303	424	486	33.1	-27
NBR:CSM+ SiO_2 (28 μm)	450	296	425	485	38.6	-28
CR	282	283	300	590	28.9	-39
CR:CSM (50:50)	466	252	326	537	16.9	-38
CR:CSM+ SiO_2 (15 nm)	463	257	349	605	30.3	-40
CR:CSM+ SiO_2 (28 μm)	465	259	361	565	32.6	-45

From the values of the temperatures at 10 % weight loss and T_{end} , it can be seen that the nano-particle sized SiO_2 filled NBR/CSM crosslinked systems (303 $^{\circ}\text{C}$, 486 $^{\circ}\text{C}$) are more stable than the micro-particle sized SiO_2 filled NBR/CSM crosslinked systems (296 $^{\circ}\text{C}$, 485 $^{\circ}\text{C}$). In the CR/CSM crosslinked systems, the temperature values at 10 % weight loss show little difference in the thermostability between the micro-particle sized SiO_2 and the nano-particle sized SiO_2 filled crosslinked systems. In the next step (30 % weight loss), the micro-filled crosslinked system had more stability than the nano-filled crosslinked system. Among the most important factors that can influence the initial TG behavior are the strength of the bonds in the main CR/CSM and NBR/CSM polymer chain and the bonds with SiO_2 .

The single glass transition temperature for the NBR/CSM and CR/CSM crosslinked systems indicates that NBR, CSM and CR are compatible. The higher values of the glass transition temperatures for the nano- than for the micro-filled crosslinked systems indicate that nano-filled crosslinking systems have greater number of $\text{SiO}-\text{C}$ link than micro-filled crosslinking systems and more stability.

Morphology microscopic studies

Scanning electron microscopic (SEM) studies of fractured surfaces were observed by scanning electron microscopy (SEM) in order to gain a better insight into the mechanism of failure of SiO₂ reinforced NBR/CSM and CR/CSM crosslinked systems. The SEM microphotographs at 2000 × magnification of the surfaces of CR/CSM polymer blends are shown in Fig. 2. The surface of the CR/CSM polymer blend with nano-SiO₂ is more polished than that with micro-SiO₂. In the microphotographs of micro-SiO₂ filled CR/CSM blend a void and a microcrack of size about 50 μm can be seen. The fractured surface of the

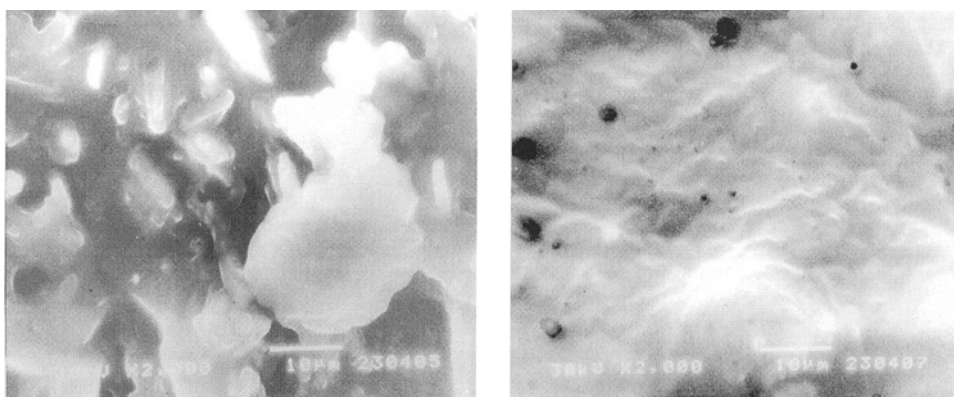


Fig. 2. SEM Microphotograph at 2000x magnification of CR/CSM rubber blends: (A) micro- SiO₂ filled; (B) nano-SiO₂ filled

micro-particle sized SiO₂ filled NBR/CSM and CR/CSM crosslinked systems becomes rougher, shows cavities, dimples and crack, in the observation region.

CONCLUSION

– The strong peak from SiO–C at 1079 cm⁻¹ in the IR spectrum of CR/CSM polymer matrix with 35 pphr SiO₂ (15 nm) suggested the presence of interaction with SiO₂ which lead to increased stability of the 35 pphr precipitated SiO₂ filled CR/CSM polymer matrix.

– Nano- silica interacts more with NBR/CSM and CR/CSM polymer matrix than micro-silica, which is the result of the greater contact area of the nano-filler, greater adsorption and lower mobility of the polymer chains or the filler surface.

– The higher values of the glass transition temperatures for the nano- than the micro-filled crosslinked systems indicate that the nano-filled crosslinked systems have a larger number of SiO–C links than micro-filled crosslinked systems and hence increased stability.

– Based on the morphological investigation of the cracked surface of NBR/CSM and CR/CSM polymer blends, can be concluded: (i) The surface of NBR/CSM polymer blends is more polished than that of CR/CSM polymer blends and without crack; (ii) the presence in both NBR/CSM and CR/CSM rubber blends with micro-particle size of SiO₂ of rubber balls and some amount of fibrosity in the matrix, voids and crazes, as well as

microcracks and crystallinity contribute towards failure of the macromolecular network structure.

– The increased number of cracks and voids in the CR/CSM polymer blends contribute to the earlier loss of physical and mechanical properties, compared to the NBR/CSM polymer blends.

ИЗВОД

ТЕРМОСТАБИЛНОСТ И МОРФОЛОГИЈА ПОВРШИНЕ НАНО- И МИКРО-ПУЊЕНИХ NBR/CSM И CR/CSM МЕШАВИНА

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Бутадиен-акрилонитрилни каучук (NBR), полихлоропренски каучук (CR), хлорсулфоновани полиетиленски каучук (CSM) и њихове мешавине умрежаване су сумпором, етилен-тиоуреом, магнезијум-оксидом или комбинацијом истих. Испитиван је утицај нано- и микро-честица SiO₂ у масеном уделу од 35 phr (део на 100 делова каучука) на термостабилност и морфологију површине умрежених система. Идентификација умрежених система на бази NBR/CSM и CR/CSM умрежених система пуњених нано- и микро-честицама SiO₂ вршена је са FTIR (Fourier transform infrared spectroscopy) са ATR (attenuated total reflectance) додатком. Термичка стабилност NBR/CSM и CR/CSM умрежених система пуњених нано- и микро-честицама SiO₂ проучавана је термогравиметријском анализом (TGA). Температура стакластог прелаза одређивана је диференцијалном сканирајућом калориметријом (DSC). Морфологија површинског прелома умрежених система одређивана је сканирајућом електронском микроскопијом (SEM). Резултати су показали да нано-честице SiO₂ са NBR/CSM и CR/CSM полимерном матрицом дају јаку траку од SiO–C на 1079 cm⁻¹. То указује на већу термичку стабилност, бољу дисперзију, сјајнију површину без напрстина и већу вредност T_g у односу на микро-пуњене NBR/CSM и CR/CSM умрежене системе.

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