

R. Rajasekar*, A. Malas* and C. K. Das*¹

Development of compatibilized butyl rubber nanocomposites containing dual filler system

This study aims in analyzing the effect of compatibilizer for the dispersion of organically modified nanoclay in butyl rubber (IIR) matrix. Chlorobutyl rubber (CIIR) – organically modified nanoclay composites (CI-C) were prepared by solution mixing. The nanoclay used in this study is Cloisite 20A. The obtained nanocomposites were incorporated in butyl rubber (IIR) along with carbon black with sulphur as a curing agent. Morphology, curing characteristics, mechanical and gas barrier properties of the nanocomposites were analysed and compared to control. The morphological studies proved the partial exfoliation along with agglomeration of nanoclay platelets in CIIR, and further incorporation of CI-C in IIR matrix enhances the exfoliation of the nanoclay platelets. Curing study demonstrated faster scorch time, cure time and increase in maximum torque for the compatibilized IIR nanocomposites containing dual filler system compared to control. Tremendous improvement in mechanical and gas barrier properties were achieved for the same system. The tensile fractured surface of the rubber compounds observed through scanning electron microscopy shows highly rough and tortuous path for the filler containing IIR compounds.

Key words: butyl rubber, compatibilizer, chlorobutyl rubber, nanocomposites, nanoclay, carbon black

Opracowanie kompatybilizowanych nanokompozytów kauczuku butylowego zawierających zespół dwóch napełniaczy

Przedstawiona praca jest ukierunkowana na przeanalizowanie wpływu środka kompatybilizującego na dyspergowanie organicznie modyfikowanego nanoglinokrzemianu w środowisku kauczuku butylowego (IIR). Kompozyty użytego jako kompatybilizatora kauczuku chlorobutylowego (CIIR) i organicznie modyfikowanego nanoglinokrzemianu (CI-C) przygotowywano przez zmieszanie składników w roztworze. Jako nanoglinokrzemianu użyto w badaniach Cloisite 20A. Uzyskane nanokompozyty wprowadzono do kauczuku butylowego (IIR) razem z sadzą i siarką jako środkiem sieciującym. Właściwości nanokompozytów – morfologiczne, wulkanizacyjne, mechaniczne i barierowe wobec gazu – analizowano i porównywano z próbką kontrolną. Badania morfologii wykazały częściową eksfoliację z jednoczesną aglomeracją płytek nanoglinokrzemianu w CIIR, a następnie wprowadzanie CI-C do matrycy IIR zwiększało eksfoliację płytek nanoglinokrzemianu. Badania wulkanizacji wykazały krótszy czas podwulkanizacji i wulkanizacji oraz wzrost maksymalnego momentu obrotowego kompatybilizowanych nanokompozytów IIR zawierających dwuskładnikowy zespół napełniaczy w porównaniu z próbką kontrolną. Stosując opisany system uzyskano ogromną poprawę właściwości mechanicznych i barierowych produktu. Powierzchnia przełomu po rozciąganiu obserwowana pod mikroskopem elektronowym okazała się bardziej szorstka i nierówna w przypadku napełnionych mieszanek IIR.

Słowa kluczowe: kauczuk butylowy, środek kompatybilizujący, kauczuk chlorobutylowy, nanokompozyt, nanoglinokrzemian, sadza

1. Introduction

The chief aim of preparing polymer-nanoclay composites is to achieve a very high degree of dispersion of nanoclay aggregates in the polymer matrix, which can yield to very large surface areas. The achievement in better

dispersion of nanoclay in the polymer matrix leads to substantial improvement in the overall properties of the polymer. Vast works have been reported on the clay filled nanocomposites based on thermoplastics and thermosetting polymers, but the studies on rubber-clay nanocomposites constitute in lesser dimension [1-3].

Butyl rubber (IIR) is made by copolymerizing isobutylene and isoprene. IIR possesses excellent resistance to gas permeation that can be applied for inner tubes in tires and air conditioner hoses, curing bags and bladders. But IIR-clay nanocomposites are not prepared easily due to the hydrophobicity of IIR and its poor miscibility with clay silicate layers. Thus, IIR-clay nanocom-

* Materials Science Centre, Indian Institute of Technology, Kharagpur-721 302, India.

¹ Corresponding Author. Tel: +91-3222-283978; Fax: +91-3222-282700/255303; E-mail address: chapal12@yahoo.co.in (Chapal Kumar Das)

posites have not received much attention. Few works have been reported by Liang et al. [4, 5] and Kato et al. [6] on the preparation of IIR-clay nanocomposites by solution and melt intercalation methods.

The achievement of better dispersion of nanoclay in the polymer matrix involves two main factors. The primary one involves the compatibility between the polymer and nanoclay. The formulas of organoclay/polymeric systems usually contain a polymeric compatibilizer [7, 8]. Since the organically modified nanoclay is polar, the utilization of polar compatibilizer may lead to better dispersion of nanoclay upon incorporation in bulk non-polar IIR matrix. As IIR is not compatible with most of other rubbers, polar chlorobutyl rubber (CIIR) was used as a compatibilizer in order to achieve better dispersion of nanoclay in the bulk IIR matrix. The secondary aspect is the method used for the preparation of nanocomposites. In this present study, incorporation of nanoclay in CIIR was done by solution mixing. The obtained CIIR-nanoclay composites (CI-C) were further incorporated in the IIR matrix in presence of carbon black with sulphur as a curing agent. The changes obtained in the morphology, curing characteristics, mechanical and gas barrier properties have been analyzed and compared to control.

2. Materials

Butyl rubber used was Lanxess Butyl 301 having Mooney viscosity $ML_{(1+8)}$ at $125^{\circ}\text{C} = 51 \pm 5$ were purchased from Lanxess.

Bayer Chlorobutyl 1240 with 1.25% chlorine content and Mooney viscosity ML_{1+8} at $125^{\circ}\text{C} = 38 \pm 4$ were purchased from Bayer.

Cloisite 20A, a natural montmorillonite modified with a quaternary ammonium salt with cation exchange capacity of 95 mequiv./100 g clay (Southern Clay, Inc., USA), was used as a nanofiller in the preparation of the nanocomposites.

Carbon black used was fast extrusion furnace black (FEF) type N550.

Other compounding ingredients such as sulphur, zinc oxide, stearic acid, *N*-cyclohexyl-2-benzothiazyl sulphenamide (CBS), Tetramethylthiuram disulphide (TMTD) were purchased from Bayer (M) Sdn Bhd Malaysia.

3. Methods

3.1. Solution mixing

Initially CIIR was dissolved in toluene. The rubber to solvent ratio was 1:3, weight/volume. Continuous stirring was done at room temperature, until the rubber dissolved completely in the solvent. Nanoclay (Cloisite 20A) containing 50 phr was separately dissolved in toluene and ultrasonicated for 10 minutes. The solution containing nanoclay was then mixed up with the rubber solu-

tion and the whole mixture was ultrasonicated for 10 minutes followed by stirring. The obtained solution was then cast over in a plane glass plate and kept at room temperature for solvent evaporation. The resultant film was appeared to be transparent.

3.2. Compounding

The compounding formulation was portrayed in Table 1. The compounds are prepared in internal mixer mill and further taken as sheet form in open two-roll mixing mill operated at room temperature. The speed ratio of the rotors was 1:1.4.

Table 1. Formulation of the rubber compounds
Tabela 1. Skład mieszanek kauczukowych

Ingredients	Designation			
	I	IB	ICB	ICCB
	Contents (phr) ^a			
Butyl rubber	100	100	100	94
Nanoclay	-	-	2.0	-
CI-C [CIIR-nanoclay composites]	-	-	-	6.0 [CIIR + Nanoclay] [4.0 + 2.0]
Carbon black FEF ^b [N550]	-	40	40	40
Stearic acid	2.0	2.0	2.0	2.0
CBS ^c	1.0	1.0	1.0	1.0
TMTD ^d	1.0	1.0	1.0	1.0
Zinc oxide	3.0	3.0	3.0	3.0
Sulphur	1.5	1.5	1.5	1.5

^a phr – Parts per hundred of rubber by weight

^b FEF – Fast extrusion furnace

^c CBS – *N*-cyclohexyl-2-benzothiazyl sulphenamide

^d TMTD – Tetramethylthiuram disulphide

Vulcanization of the rubber compounds was done in the compression molding machine at 150°C , as per the optimum cure time obtained from Monsanto Rheometer study.

4. Characterization techniques

4.1. X-ray diffraction

The clay gallery height was analyzed using a Philips PANalytical X'pert PRO X-ray diffractometer instrument with $\text{Cu-K}\alpha$ radiation. The generator voltage and wavelength was 40 kV and 0.154 nm at room temperature respectively. The crystallographic spacing (*d*) of the nanoclays was calculated from the Bragg's law. The range of 2θ scanning of X-ray intensity employed was $2 - 10^{\circ}$ at a scanning rate of 2°min^{-1} .

4.2. High resolution transmission electron microscopy (HR-TEM)

The morphology of nanoclay dispersion in CIIR (i.e., CI-C) and IIR matrices in presence of carbon black (i.e., IB, ICB and ICCB) were observed through high-resolution transmission electron microscope (HR-TEM, JEOL 2100). Sample preparation was done in Leica Ultra cut UCT ultramicrotome equipped with a diamond knife. The thickness of the ultra thin specimens was approximately 80 nm and the temperature of the samples was maintained at $-70\text{ }^{\circ}\text{C}$ with the help of liquid nitrogen. These samples were then placed on the copper grid.

4.3. Cure characteristics

The cure characteristics of the compounds were studied in the Monsanto Rheometer R-100 testing instrument operated at $150\text{ }^{\circ}\text{C}$ with 3° arc at a period of 60 minutes.

4.4. Mechanical testing

Dumbbell and crescent shaped specimens were cut down for tensile and tear tests from the molded slabs. The testing was carried out from Universal tensile testing machine, Hounsfield HS 10 KS model operated at room temperature at an extension speed of 500 mm/min with an initial gauge length of 25 mm. The values of are recorded directly from the digital display at the end of each test.

4.5. Permeability measurements

The gas transport properties of the pure, single and dual filler filled IIR compounds were analysed. Nitrogen gas XL grade gas purchased from BOC Gases, India was used for the measurement. The gas was applied at a constant pressure of 3.5 bar at $35\text{ }^{\circ}\text{C}$ with a time period of 30 minutes using the automated Diffusion Permeameter (DP-100-A) manufactured by Porous Materials, Inc., USA. The permeation equipment was placed in a thermostatically controlled housing for isothermal measurement conditions. The effective permeation area (A) was 5.069 cm^2 . The nitrogen gas was supplied from the upstream side of the film with a gas pressure of 3.5 bar (p_i) and in the downstream side a reservoir of constant volume (119 cm^3) was connected with a pressure transducer in order to monitor the total amount of gas that gets passed through the polymer film. The time lag method was used to calculate the gas transport measurements. This technique allows the determination of the mean permeability coefficient (P) from the steady state gas pressure increment $(dp/dt)_s$ in the calibrated volume V of the product side of the cell. The permeability coefficients were calculated from Eq. (1), where T_0 and p_0 are the standard temperature and pressure ($T_0 = 273.15\text{ K}$, $p_0 =$

1.013 bar), T is the temperature of measurement, d is the thickness of the film and $(dp/dt)_s$ was obtained from the slope of the increments of downstream pressure vs. time plot. The mean permeability (P) [9] was calculated from Eq. (1).

$$P = \frac{VdT_0}{Ap_i p_0 T} \left[\frac{dp}{dt} \right]_s \quad (1)$$

The effective diffusion coefficient (D) [9] was calculated from the time-lag according to the following Eq. (2):

$$D = \frac{d^2}{6\theta} \quad (2)$$

4.6. Scanning electron microscopy

The morphology of tensile fractured surface was viewed through scanning electron microscope (SEM, VEGA TESCAN). Gold coating was done under vacuum condition to prevent electrostatic charge while examining.

5. Results and discussions

5.1. X-ray diffraction

The XRD patterns of the nanocomposites were shown in figure 1. The nanoclay (Cloisite 20A) depicted an intense peak around $2\theta = 3.144^{\circ}$, corresponding to the basal spacing 2.82 nm (d_{001}). 50 phr incorporation of nanoclay in CIIR [CI-C] by solution phase mixing showed the disappearance of the main peak of the nanoclay. Although a secondary peak arise at 6.48° corresponding to the basal spacing of 1.37 nm . This proved that the nanoclay platelets are partially exfoliated as well as agglomerated in the CIIR matrix, which may be due to higher

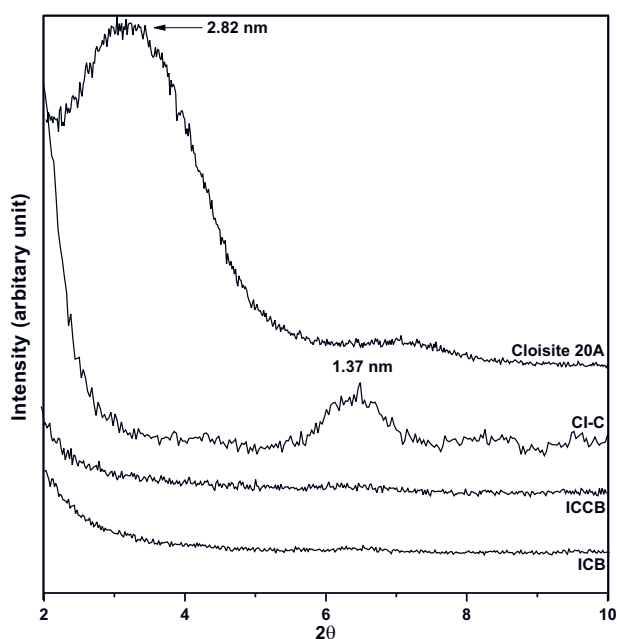


Figure 1. XRD pattern of the nanocomposites
Rys. 1. Dyfraktogramy XRD nanokompozytów

nanoclay loading in CIIR. Further incorporation of CI-C in IIR matrix (ICCB) along with carbon black showed complete absence of peaks. As the loading of CI-C in IIR matrix is low, the exfoliation of nanoclay may be more enhanced in the bulk IIR matrix. The compound ICB containing nanoclay incorporation in IIR containing carbon black without compatibilizer does not show any peak. This also proved that the nanoclay may be partially exfoliated in the IIR matrix.

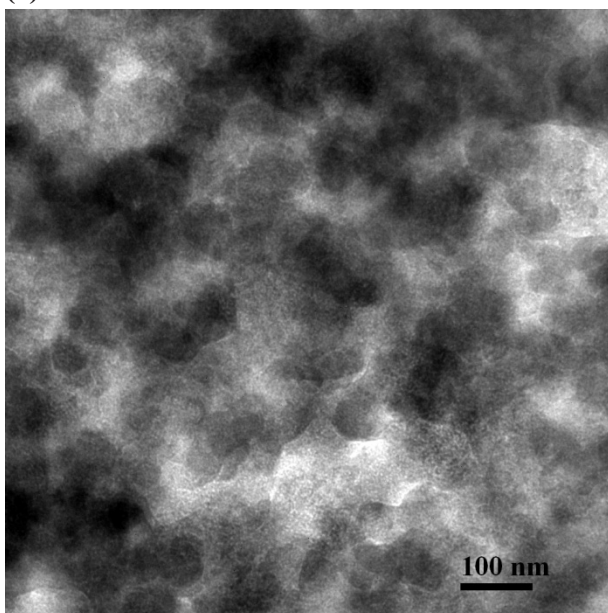
Since the organically modified nanoclay is polar, the utilization of polar compatibilizer CIIR may form a better dispersion of nanoclay upon incorporation in the

non-polar IIR matrix, than direct incorporation of polar nanoclay in the non-polar matrix polymer.

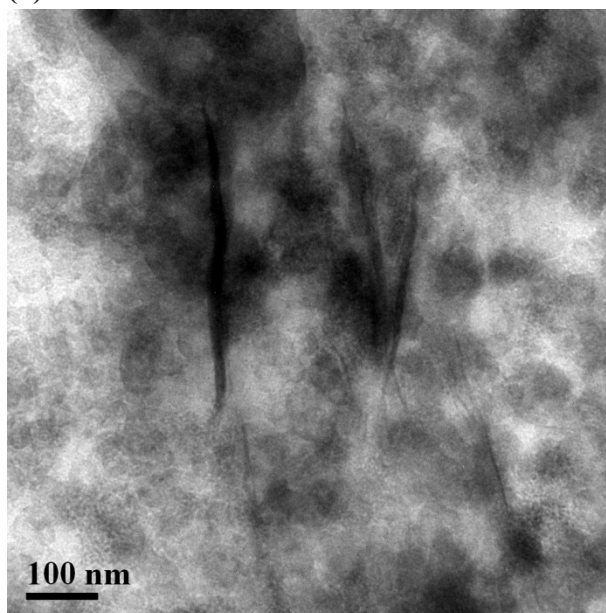
5.2. HR-TEM analysis

HR-TEM images of the nanocomposites were shown in figures 2 (a) IB, (b) ICB, (c) CI-C (d) ICCB respectively. Figure IB shows the cluster of carbon black dispersed throughout the IIR matrix. ICB shows the presence of dual fillers (i.e., nanoclay and carbon black) in the IIR, in which the nanoclay platelets were partly exfoliated and also agglomerated. CI-C shows numerous nanoclay pla-

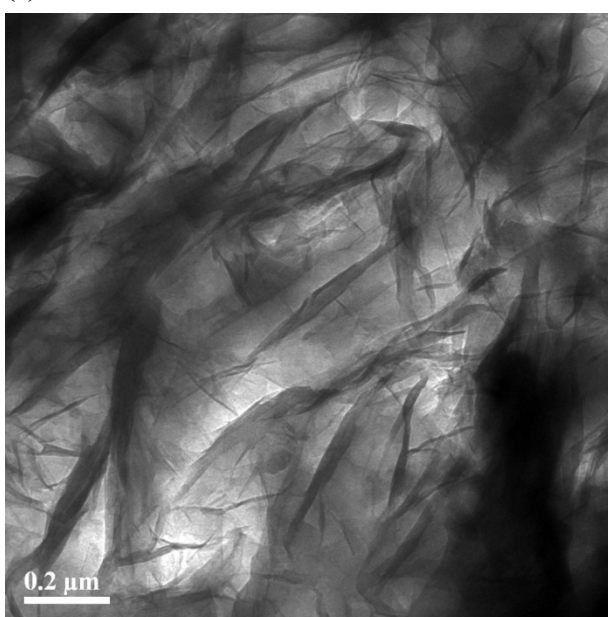
(a) IB



(b) ICB



(c) CI-C



(d) ICCB

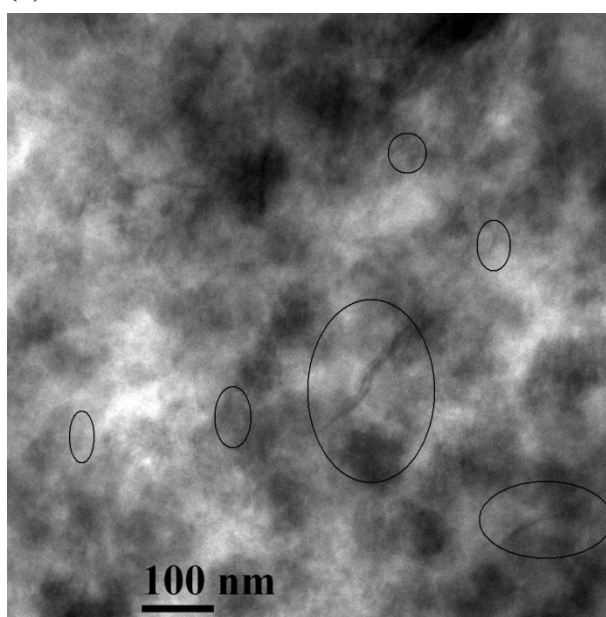


Figure 2. TEM images of (a) IB, (b) ICB, (c) CI-C, (d) ICCB
Rys. 2. Obraz TEM nanokompozytów

Table 2. Cure characteristics of the rubber compounds

Tabela 2. Charakterystyka wulkanizacji mieszanek kauczukowych

Sample code	Min. Torque (dN·m)	Max. Torque (dN·m)	Torque difference (dN·m)	Scorch time (min)	Cure time (min)	Cure rate index
I	10.5	36	25.5	6.00	22.00	6.25
IB	11.5	42.5	31	4.00	19.30	6.53
ICB	12	43.5	31.5	3.00	18.30	6.53
ICCB	12	44	32	3.00	18.00	6.66

telets scattered in CIIR matrix. Since the content of nanoclay is 50 phr in CIIR, some platelets were stacked and few are exfoliated. Figure ICCB shows enhanced dispersion of nanoclay forming partially exfoliated platelets in comparison with ICB. The circular spots denote the presence of nanoclay platelets. This may be due to the utilization of polar compatibilizer (CIIR) for dispersing nanoclay in the IIR matrix.

5.3. Cure characteristics

The cure characteristics of the rubber compounds are shown in table 2.

The compound IB shows improvement in minimum and maximum torque value compared to IIR gum compound (I). The improvement may be due to the presence of carbon black in the IIR matrix (IB). The maximum torque depends on both the extent of crosslinking and reinforcement by the filler particles in the polymer matrix. This enhancement was further pronounced for the IIR compounds containing nanoclay and carbon black (ICB and ICCB). Particularly the compound ICCB showed the maximum improvement in torque values than ICB. The improvement may be due to the presence of compatibilizer (CIIR) that enhances the dispersion of the nanoclay in the base polymer matrix. The carbon black filled IIR compound showed faster scorch and cure time compared to the unfilled IIR compounds. Normally, the carbon black filled rubber compounds have faster scorch and cure time compared to the gum compounds. Carbon black facilitates the opening of the S_8 rings even in the absence of accelerators and it enhances the formation of H_2S , which activates most sulphur curing systems. It seems that carbon black supports vulcanization reactions without changing their nature substantially [10]. The dual filler containing IIR compounds showed faster scorch and cure time compared to the unfilled and single filler containing IIR systems. Apart from the presence of carbon black, the presence of ammonium groups in the organically modified nanoclay may also facilitates the process. The possible formation of a Zn complex in which sulfur and ammonium modifier participate may help for the increase in rate of cure. Hence, depending upon the ammonium concentration in the nanoclay greater will be the chance of Zn-sulfur-ammonium complex formation in the nanocomposites and consequently faster scorch time and cure time were achieved [11].

5.4. Mechanical properties

The mechanical properties of the rubber compounds are shown in figure 3 (a) & (b).

The compound IB containing single filler (carbon black) in IIR matrix showed tremendous improvement in mechanical properties compared to the unfilled IIR compound (I). The increase in tensile and tear strength are 600 % and 270 %. The enhancement was further pronounced for the systems (ICB and ICCB) containing dual fillers. The compound ICB showed 770 % increase in tensile and 296 % increase in tear strength, whereas

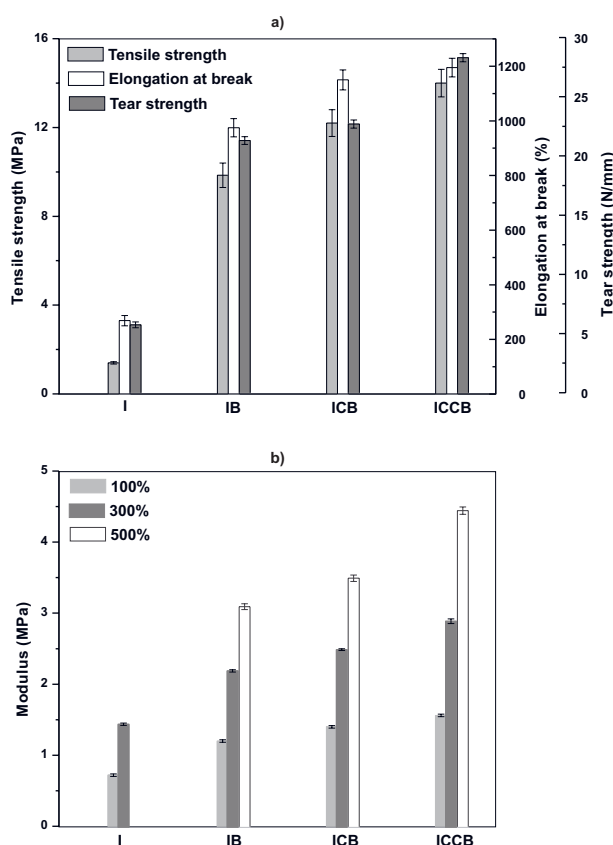


Figure 3. (a) Tensile, elongation at break and tear strength of the rubber compounds, (b) 100% and 300% modulus of the rubber compounds

Rys. 3. (a) Wytrzymałość na rozciąganie, wydłużenie przy zerwaniu i wytrzymałość na rozdzieranie (wulkanizatów) mieszanek kauczukowych, (b) moduł 100% i 300% (wulkanizatów) mieszanek kauczukowych

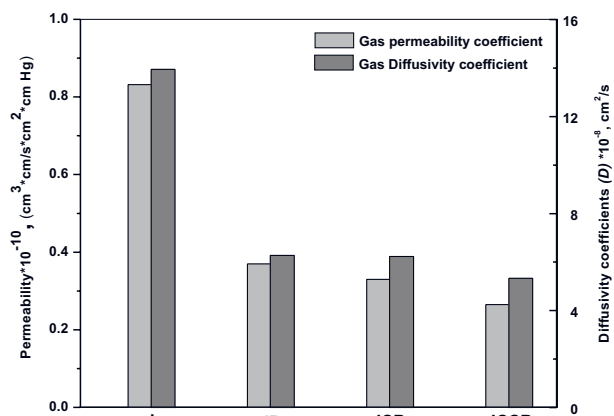


Figure 4. Permeability and diffusivity coefficient of the rubber compounds

Rys. 4. Przenikalność i współczynnik dyfuzji (wulkanizatów) mieszanek kauczukowych

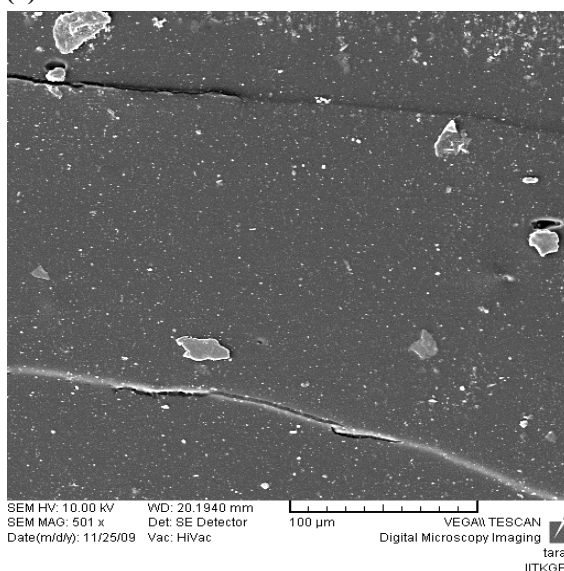
the compound ICCB showed an increase of 900 % in tensile strength and 394 % increase in tear strength respectively. This proved that the presence of compatibilizer may improve the dispersion of the nanofiller in the matrix polymer.

5.5. Gas barrier properties

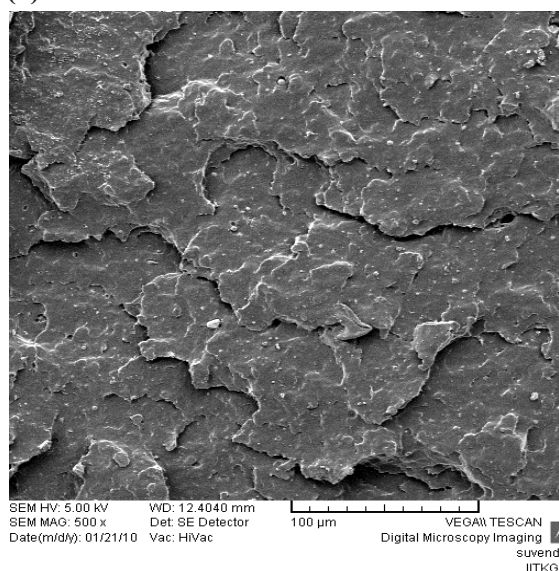
The gaseous permeability and diffusivity coefficient of the compounds are shown in figure 4.

The compound IB showed lower gas permeability compared to I. The lower gas permeability may be due to the presence of carbon black. The gas permeation was still reduced for the compounds ICB and ICCB compared to unfilled and carbon black filled IIR compounds. This may be due to the presence of dual fillers that forms

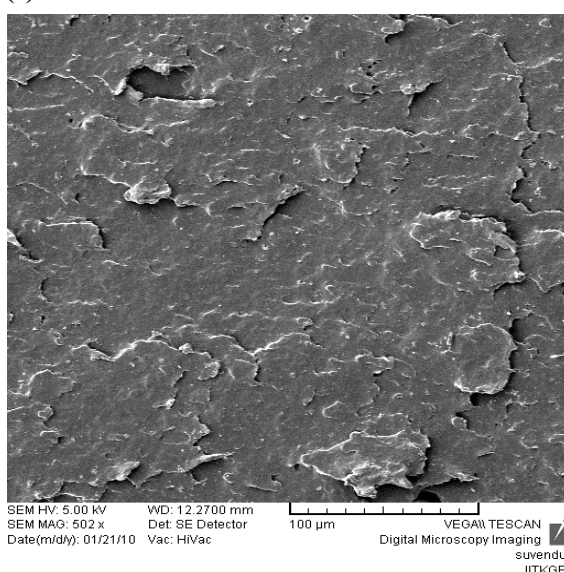
(a) I



(b) IB



(c) ICB



(d) ICCB

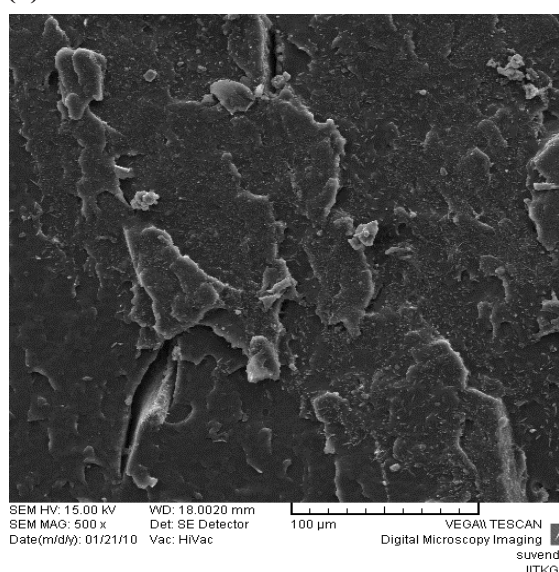


Figure 5. SEM images of (a) I, (b) IB, (c) ICB, (d) ICCB

Rys. 5. Obrazy SEM próbek (a) I, (b) IB, (c) ICB, (d) ICCB

a strong barrier for the penetration of nitrogen gas through the rubber compound. The lowest gas permeability was observed for the compound ICCB. The exfoliation of nanoclay platelets forming a strong interaction with the matrix polymer may be responsible for the meandering of the nitrogen gas diffusion paths, drawing nitrogen molecules to follow long, complex paths through the IIR matrix, hence decreasing the permeability [6]. The diffusivity coefficient also showed the similar trend to that of permeability coefficient for the above mentioned compounds. The better dispersion of nanoclay in the compound ICCB reduces the diffusivity by increasing the tortuosity of the gas transport path [12].

5.6. Scanning electron microscopy

The SEM images of the tensile fractured surfaces were shown in figure 5 (a) I, (b) IB, (c) ICB and (d) ICCB.

In comparison to the unfilled IIR compound (I), the compounds IB, ICB, and ICCB containing single and dual fillers in the IIR matrix showed highly rough and tortuous path of fracture. This may be due to better interaction between the filler and the rubber matrix. The dispersion of fillers in the IIR matrix alters the crack path along their length depending on their orientation in the matrix. Hence, it forms more resistance to crack propagation as a result higher tensile strength.

6. Conclusion

The morphological studies proved the partial exfoliation of nanoclay in CIIR and incorporation of CIIR-nanoclay in IIR matrix further enhanced the exfoliation of nanoclay platelets. The curing study showed faster scorch time, cure time and increase in maximum torque for the compatibilized nanoclay filled IIR compound compared to control. Further these particular compounds showed superior technical and gas barrier properties. SEM images of the tensile fractured surfaces depicted increase in roughness and tortuous path for the single and dual filler containing IIR compounds.

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