

Elastomeric nanocomposites based on EPR and oil extended EPDM

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The crucial factor that decides the improvement of properties in rubber by the incorporation nanofiller, is its distribution in the rubber matrix. The normal mixing of non polar rubber and organically modified nanoclay may not lead for the exfoliation of the filler in the rubbery matrix. Hence, some sort of polar rubber like epoxidized natural rubber (ENR) can be used as a compatibilizer, in order to obtain a better dispersion of the nanoclay in the matrix polymer. Epoxidized natural rubber and organically modified nanoclay composites (EC) were prepared by solution mixing. The nanoclay used in this study is Cloisite 20A. The obtained nanocomposites were incorporated in the oil-extended ethylene propylene diene monomer (OE-EPDM) with sulphur as a curing agent and also in ethylene propylene rubber (EPR) containing dicumyl peroxide curing system. The morphological studies proved the intercalation of nanoclay in ENR and further incorporation of EC in OE-EPDM and EPR matrix leads to exfoliation of the nanoclay. Curing study demonstrated faster scorch time, cure time and increase in maximum torque for the nanoclay incorporated OE-EPDM and EPR compounds compared to their controls. Dynamic mechanical thermal analysis showed increase in storage modulus and lesser damping characteristics for the compounds containing nanoclay loading in OE-EPDM and EPR matrices, accompanied by improvements in other technical properties.

Key words: nanocomposites, epoxidized natural rubber (ENR), nanoclay, oil-extended ethylene propylene diene monomer (OE-EPDM), ethylene propylene rubber (EPR).

Nanokompozyty elastomerowe z EPR i modyfikowanego olejem EPDM

Czynnikiem decydującym o poprawie właściwości gumy przez dodatek nanonapełniacza jest jego zdyspergowanie w ośrodku kauczukowym. Zwykłe mieszanie niepolarnego kauczuku i nanoglinokrzemianu modyfikowanego substancją organiczną może nie doprowadzić do eksfoliacji napełniacza w matrycy kauczukowej. Dlatego, w celu uzyskania jego lepszej dyspersji w kauczuku, można zastosować jako kompatybilizator polarny, epoksydowany kauczuk naturalny (ENR).

Kompozyty (EC) epoksydowanego kauczuku naturalnego i organicznie modyfikowanego nanoglinokrzemianu (Cloisite 20A) przygotowywano przez mieszanie w roztworze. Uzyskane nanokompozyty wprowadzono do EPDM modyfikowanego olejem (OE-EPDM), z siarką jako środkiem wulkanizującym oraz do kauczuku etylenowo-propylenowego (EPR) zawierającego zespół wulkanizujący z nadtlakiem dikumylu. Badania morfologiczne potwierdziły interkalację nanoglinokrzemianu w ENR, a następnie jego eksfoliację po wprowadzeniu EC do OE-EPDM lub EPR. W badaniu procesu wulkanizacji stwierdzono szybszą podwulkanizację i krótszy czas wulkanizacji oraz wzrost maksymalnego momentu reometrycznego mieszanek OE-EPDM i EPR zawierających dodatek nanoglinokrzemianu w stosunku do mieszanek kontrolnych. Badania DMTA wykazały wzrost składowej rzeczywistej modułu zespolonego oraz słabsze właściwości tłumiące mieszanek OE-EPDM i EPR zawierających EC, towarzyszyła temu poprawa innych właściwości technicznych.

Słowa kluczowe: nanokompozyty, epoksydowany kauczuk naturalny (ENR), nanoglinokrzemian, terpolimer etylenowo-propylenowo-dienowy modyfikowany olejem (OE-EPDM), kauczuk etylenowo-propylenowy (EPR)

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1. Introduction

The main objective in preparing organoclay nanocomposites is to achieve a better degree of dispersion of organoclay aggregates in the polymer matrix, which can yield to very large surface areas. This in turn remarkably enhances the overall properties of the nanocomposites. Vast works have been done in clay filled nanocomposites for many thermoplastics and thermosetting polymers. But the studies on rubber based nanocomposites constitute in lesser dimension [1-4].

The accomplishment of good dispersion of organoclay nanocomposites involves two main aspects. The primary one involves the compatibility between the polymer and nanoclay. The organically modified nanoclay which is polar may not contribute for the better dispersion upon direct incorporation in the non-polar rubber matrices like ethylene propylene rubber (EPR) and oil-extended ethylene propylene diene monomer (OE-EPDM). Hence a polar rubber, which is compatible with the matrix polymer can be used as a compatibilizer, for the better dispersion of nanoclay in the non-polar rubber matrices. Epoxidized natural rubber (ENR) obtained by epoxidation of 1,4-polyisoprene, depicts higher glass transition temperature, increased polarity and have a better compatibility with EPR and OE-EPDM. Hence, ENR was chosen as a compatibilizer in this study. Few good works have been done by Arroyo et al [5], P. L. Teh et al [6] and S. Varghese et al [7] using ENR as compatibilizer for organoclay/natural rubber nanocomposites. From our laboratory, we have already analyzed the effect nanoclay composites using ENR as a compatibilizer in few rubber matrices like natural rubber [8,9], styrene butadiene rubber [10] and nitrile butadiene rubber [11].

The secondary one is the method used for the preparation of nanocomposites. It includes insitu polymerization intercalation [12], solution intercalation [13], melt intercalation [6], finally co-coagulation of rubber latex and clay aqueous suspension [14].

In this present study, incorporation of nanoclay in ENR was done by solution mixing. The obtained ENR-nanoclay composites (EC) were incorporated in the EPR containing dicumyl peroxide curing system and OE-EPDM cured with sulphur. The changes obtained in the morphology, curing characteristics and mechanical properties have been analyzed and compared to that of their respective controls.

2. Materials

Ethylene propylene rubber used was Vistalon – 719 procured from Exxon Chemical, USA. (ethylene 60%, propylene 40%).

Oil-extended ethylene propylene diene terpolymer was Keltan 5531A obtained from DSM Elastomer B.V., The Netherlands. (ethylene 63%, Ethylidene norbornene (ENB) 4.5%, paraffinic oil 50 wt%)

Epoxidized natural rubber containing 50 mol% epoxidic units was supplied from Agricultural Product Processing Research Institute, Zhangiang, PR China.

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.

Other compounding ingredients such as sulphur, zinc oxide, stearic acid, *N*-cyclohexyl-2-benzothiazyl sulphenamide (CBS), tetramethylthiuram disulphide (TMTD), triallyl cyanurate (TAC) and dicumyl peroxide (DCP) were purchased from Bayer (M) Sdn Bhd Malaysia.

Table 1. Formulation of the rubber compounds

Tabela 1. Skład mieszanek kauczukowych

Ingredient	EPR	EPR/5EC	EPR/10EC	OE-EPDM	OE/5EC	OE/10EC
Content (phr ^a)						
Ethylene propylene rubber	100	95	90	—	—	—
Oil-extended ethylene propylene diene terpolymer	—	—	—	100	95	90
EC ^b	—	5	10	—	5	10
Stearic acid	—	—	—	1	1	1
CBS ^c	—	—	—	1	1	1
TMTD ^d	—	—	—	0.5	0.5	0.5
Zinc oxide	—	—	—	3	3	3
Sulphur	—	—	—	1.5	1.5	1.5
TAC ^e	0.2	0.2	0.2	—	—	—
DCP ^f	1	1	1	—	—	—

^a phr – Parts per hundred of rubber by weight, ^b EC – ENR-nanoclay composites, ^c CBS – *N*-cyclohexyl-2-benzothiazyl sulphenamide, ^d TMTD – Tetramethylthiuram disulphide, ^e TAC – Triallyl cyanurate, ^f DCP – Dicumyl peroxide

3. Methods

3.1. Solution mixing

ENR was dissolved in toluene. The ratio of the rubber to solvent was 1:3, weight/volume. The rubber solution was continually stirred at room temperature, until the rubber dissolved completely in the solvent. Then 50 phr of nanoclay (Cloisite 20A) was added to the rubber solution under continuous stirring. The whole mixture was ultrasonicated for 30 minutes, then casted over in a plane glass plate and kept in the same condition until the solvent evaporated completely. The obtained film was transparent.

3.2. Compounding

The formulation of the rubber compounds are shown in Table 1. The compounding was done in open two-roll mixing mill operated at room temperature. The speed ratio of the rotors was 1:1.4. The rubber compounds were vulcanized in the compression molding machine at 150 °C, concurring to the optimum cure time obtained from Monsanto Rheometer.

4. Characterization techniques

4.1. Cure characteristics

The curing study was carried out for the compounds in the Monsanto Rheometer R-100 testing instrument operated at 150 °C with 3° arc at a period of 60 minutes.

4.2. X-ray diffraction

The clay gallery height was determined using an X-ray diffractometer (Philips PANalytical X'pert PRO) with Cu-K α radiation at a generator voltage of 40 kV and wavelength of 0.154 nm at room temperature. The crystallographic spacing (d) of the nanoclay were calculated using Bragg's law. The range of 2θ scanning of X-ray intensity employed was 1.5 – 10° with a scanning rate of 2° min⁻¹.

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

The dispersion morphology of nanoclay in ENR (EC), EC incorporated in EPR and OE-EPDM matrices are observed in the high-resolution transmission electron microscope (TEM, JEOL 2100). The ultra-thin cross-sections of the specimens were prepared using a

Leica Ultra Cut UCT ultramicrotome instrument equipped with a diamond knife. The thickness of the HR-TEM specimens were approximately 80 nm and the temperature of the samples was maintained at -60 °C using liquid nitrogen for sample processing. These samples were then placed on the copper grids.

4.4. Dynamic mechanical thermal analysis

Dynamic mechanical properties of the compounds are analyzed using a TA Instrument DMA 2980 model in tension mode. The samples are subjected to a sinusoidal displacement of 0.1 % strain at a frequency of 1 Hz between the temperatures ranging from -80 °C to 80 °C at a heating rate of 3 °C min⁻¹. The storage modulus (E') and loss tangent ($\tan \delta$) of the compounds are analyzed.

4.5. Mechanical testing

Dumbbell and crescent shaped specimens for tensile and tear tests are cut down from the molded slabs. Tensile strength was done according to ASTM D-412-06 and tear strength was determined according to ASTM D-624-00(2007) and the study was carried out in a 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 are recorded directly from the digital display at the end of each test.

4.6. Scanning electron microscopy

The morphology of tensile fractured surface samples was examined through scanning electron microscope (SEM, VEGA TESCAN). In order to prevent electrostatic charge while examining, gold coating was done on the samples under vacuum condition.

5. Results and discussions

5.1. X-ray diffraction analysis

The XRD patterns of pure nanoclay, EC, OE/5EC, OE/10EC, EPR/5EC and EPR/10EC are shown in figure 1. The nanoclay (Cloisite 20A) shown an intense peak around $2\theta = 3.144^\circ$, corresponding to the basal spacing of 2.82 nm (d_{001}). The EC pattern showed the shifting of the d_{001} main diffraction peak towards the lower angle $2\theta = 2.29^\circ$, corresponding to the basal spacing of 3.87 nm (d_{001}). This proved the intercalation of nanoclay in the ENR. Moreover, in addition to the main peak, one accompanying peak at $2\theta = 4.55^\circ$ corresponding to the basal spacing of 1.94 nm (d_{002}) arises, which may be due to some re-aggregation of nanoclay

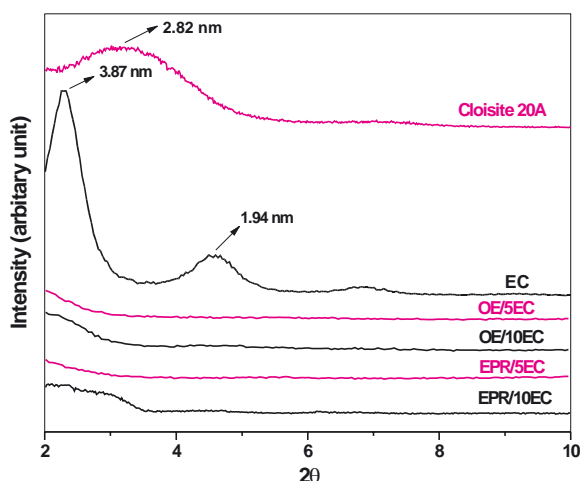


Figure 1. XRD of pure nanoclay (Cloisite 20A), EC, OE/5EC, OE/10EC, EPR/5EC and EPR/10EC.
Rysunek 1. Rentgenografia dyfrakcyjna (XRD) czystego glinokrzemianu (Cloisite 20A), EC, OE/5EC, OE/10EC, EPR/5EC i EPR/10EC

Table 2. Cure characteristics
Tabela 2. Charakterystyka wulkanizacji

Sample code	Min. torque (dNm)	Max. torque (dNm)	Torque difference (dNm)	Scorch time (min)	Cure time (min)	Cure rate index
EPR	11	61.0	50.0	5.00	25.00	5.00
EPR/5EC	11.5	65.5	54.0	4.00	21.30	5.78
EPR/10EC	12	68.0	56.0	3.30	19.30	6.25
OE	7.0	30.0	23.0	4.00	20.00	6.25
OE/5EC	7.5	33.0	25.5	2.00	17.00	6.66
OE/10EC	8.0	36.5	28.5	1.45	15.00	7.38

layers in the ENR. The secondary peak diminishes relatively to the main peak, which confirms the presence of an intercalated structure [15]. Incorporation of 5 and 10 phr of EC in OE-EPDM (OE/5EC and OE/10EC) showed the absence of peaks, suggesting the exfoliation of nanoclay in the rubber matrix. In case of EPR system, the 5 phr addition of EC (EPR/5EC) leads to absence of peaks, which proves that the nanoclay had been exfoliated in EPR system. Further increase in addition of EC to 10 phr showed the formation of a broad and weak diffraction peak suggesting the combined intercalated/exfoliated structure due to higher nanoclay loading in the EPR matrix. [16].

5.2. HR-TEM analysis

HR-TEM images for the nanocomposites are depicted in figure 2(a-e) for EC, EPR/5EC, EPR/10EC, OE/5EC and OE/10EC respectively. Clusters of nanoclay can be seen in the EC image, in which the dark lines represent the silicate layers. It proves that bulks of nanoclay dispersion are in the intercalated state, which confirms the better dispersion of nanoclay in ENR. The

figures 2(b) showed the homogeneous dispersion of nanoclay platelets that are disorderly oriented in throughout the EPR matrix. Figure 2(c) showed combined intercalated and exfoliated morphology of the nanoclay platelets due to increase in loading of nanoclay. Figures 2(d&e) also demonstrates the homogeneous dispersion of nanoclay platelets in the OE-EPDM matrix. The cylindrical black spots found in the image 2(d) may be the presence of ZnO particles. The better dispersion of nanoclay in both the rubbers proved the better compatibility of ENR with the matrix polymers.

5.3. Cure characteristics

The cure characteristics of the rubber compounds are shown in Table 2. The minimum torque value showed a slender increase for the nanoclay filled compounds than of the pure ones. The maximum torque increased with the gradual increase in loading of nanoclay in both the EPR and OE-EPDM matrices. The increase in maximum torque may be due to the exfolia-

tion of the nanoclay platelets that contributes for the higher reinforcing efficiency of the filler particles in the polymer matrix.

Faster scorch and cure time are observed for the compounds containing nanoclay composites in the EPR and OE-EPDM matrices than that of the pure ones. The gradual increase in loading of nanofiller in both the rubber matrices may be responsible for faster scorch time and cure time than that of the controls.

5.4. Dynamic mechanical thermal properties

Figures 3 (a-d) represented the temperature dependence of dynamic storage modulus (E') and loss factor ($\tan \delta$) respectively. The compounds containing nanoclay loading showed tremendous improvement in storage modulus values compared to that of the controls. At 25 °C, the compounds EPR/5EC and EPR/10EC showed 47 % and 76 % increase in storage modulus compared to pure EPR. Also the compounds OE/5EC and OE/10EC depicted 43 % and 80 % en-

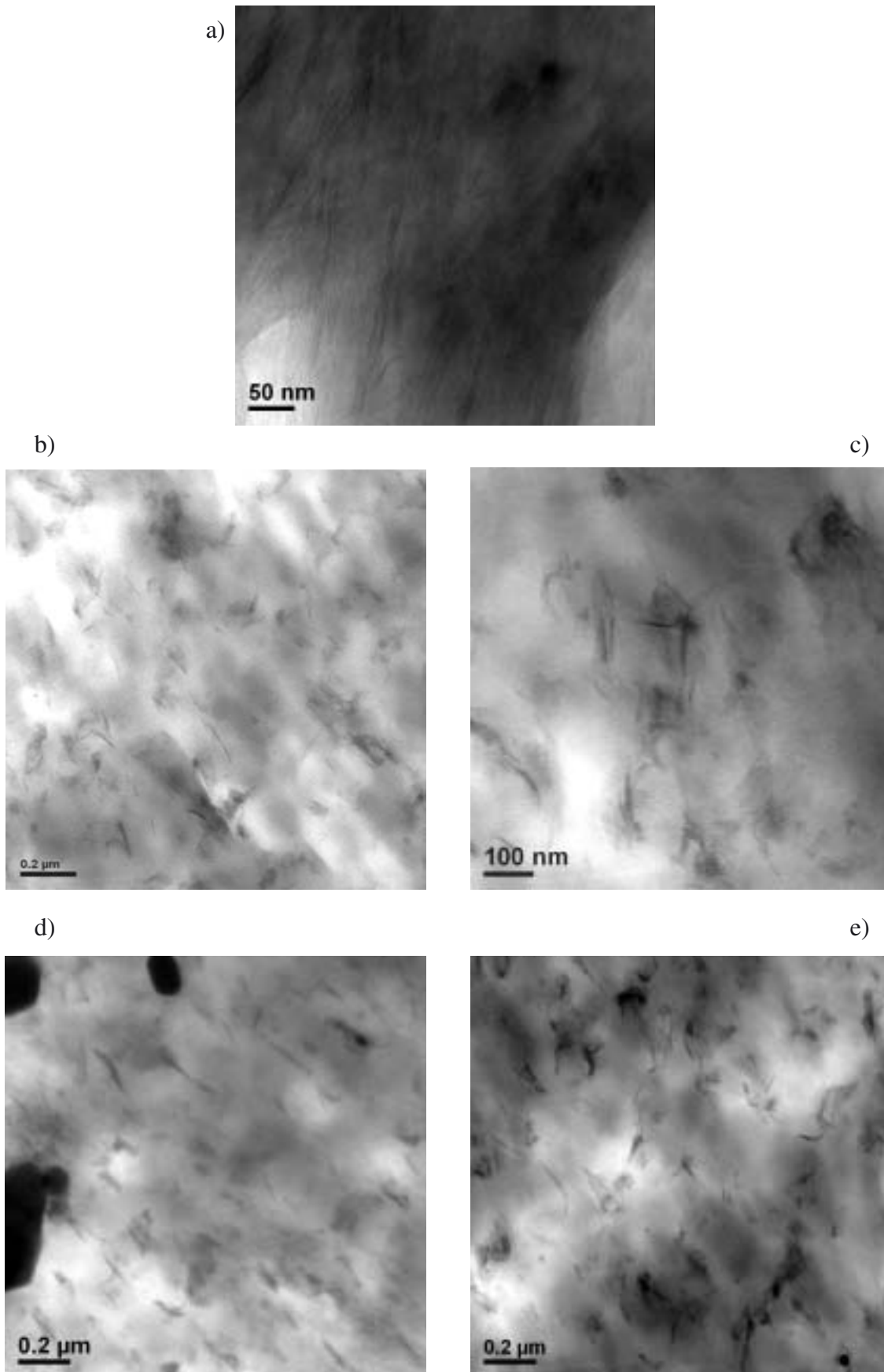


Figure 2. TEM images of (a) EC, (b) EPR/5EC, (c) EPR/10EC, (d) OE/5EC and (e) OE/10EC.

Rysunek 2. Zdjęcia TEM: (a) EC, (b) EPR/5EC, (c) EPR/10EC, (d) OE/5EC i (e) OR/10EC

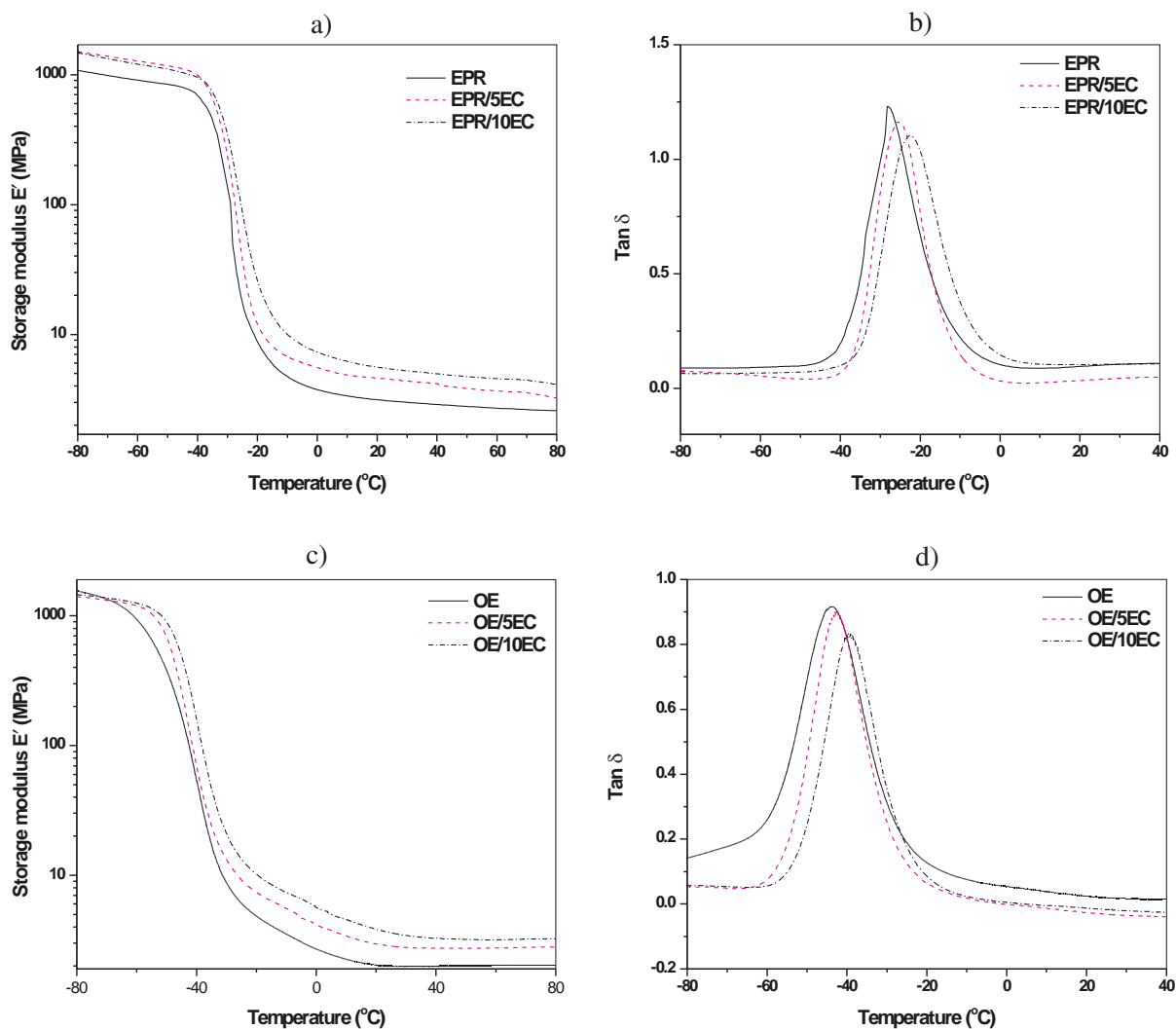


Figure 3. (a) Storage modulus (b) $\tan \delta$ of EPR, EPR/5EC and EPR/10EC (c) Storage modulus (d) $\tan \delta$ of OE, OE/5EC and OE/10EC

Rysunek 3. (a) Składowa rzeczywista modułu zespolonego i (b) $\tan \delta$ EPR, EPR/5EC, EPR/10EC, (c) składowa rzeczywista modułu zespolonego i (d) $\tan \delta$ OE, OE/5EC, OE/10EC

Table 3. Mechanical properties

Tabela 3. Właściwości mechaniczne

Sample code	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100 %	Modulus at 300 %	Tear strength (N/mm)
EPR	1.27	350	0.95	1.27	7.35
EPR/5EC	2.10	681	1.45	1.77	11.2
EPR/10EC	2.50	521	1.67	2.05	13.5
OE	1.20	150	0.65	—	4.45
OE/5EC	1.72	393	0.97	1.32	7.40
OE/10EC	2.10	524	1.30	1.84	10.00

hancement in the storage modulus values in comparison to that of the control.

Incorporation of nanoclay in both the rubber matrices showed decrease in $\tan \delta$ peak. This phenomenon proceeds with further decrease in $\tan \delta$ peak upon in-

crease in nanoclay loading compared to pure ones. This corresponds to reinforcing tendency of the nanofiller in the matrix. Restriction in the chain mobility owing to physical and chemical adsorption of the rubber molecules on the filler surface causes reduction in height of

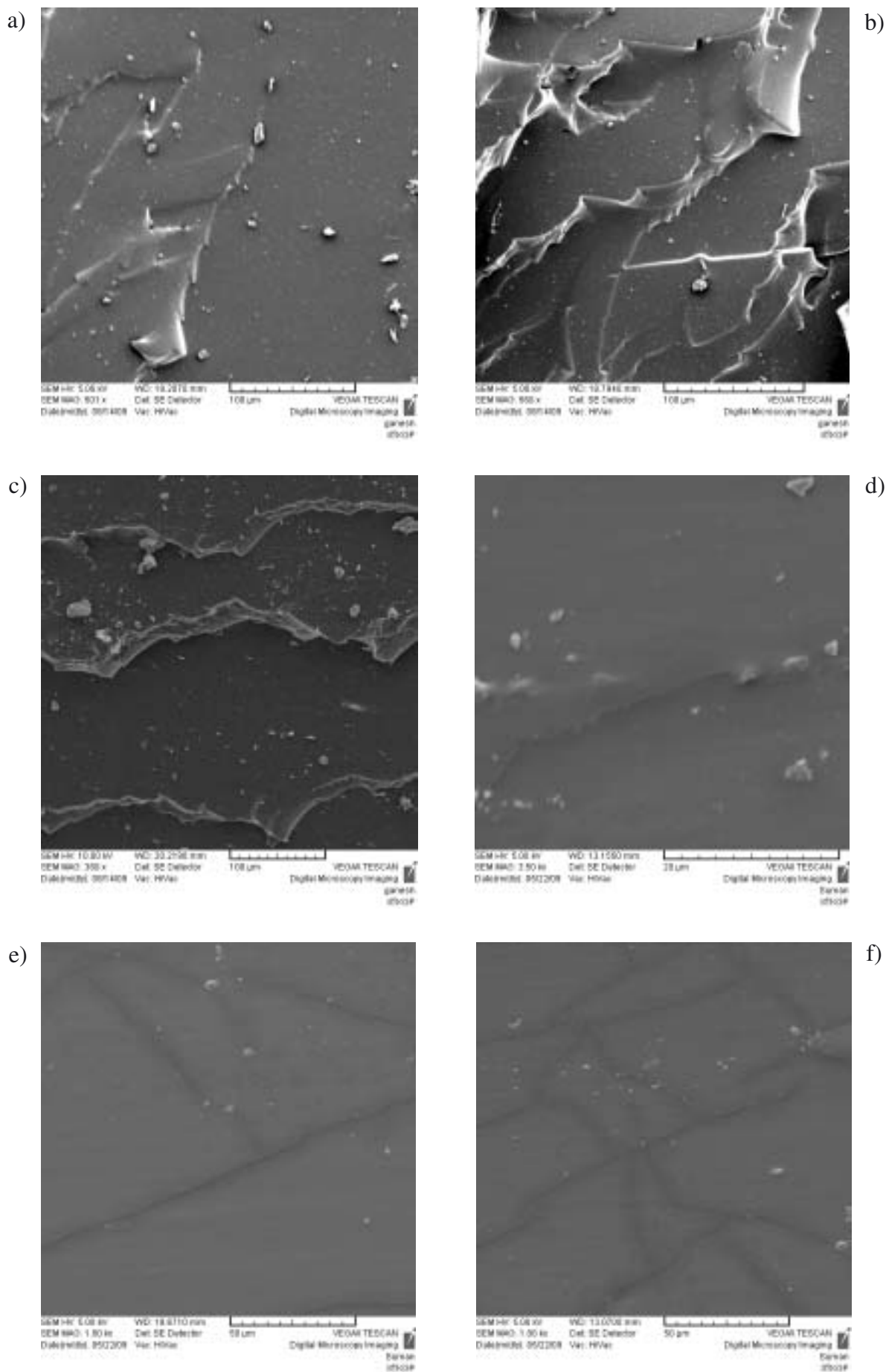


Figure 4. SEM images of (a) EPR (b) EPR/5EC, (c) EPR/10EC, (d) OE, (e) OE/5EC, (f) OE/10EC.
 Rysunek 4. Zdjęcia SEM (a) EPR, (b) EPR/5EC, (c) EPR/10EC, (d) OE, (e) OE/5EC, (f) OE/10EC

tan δ peak during dynamic mechanical deformation [17]. The decrease in tan δ peak proves lesser heat buildup and as a result lesser damping characteristics for the compounds containing nanoclay composites. The incorporation of nanoclay showed increase in glass transition temperature compared to pure ones. This may be due to the strong interactions between the nanolayers and the matrix polymer that restrict the movement of polymer chains near to the filler surface, and hence results in an increase of the glass transition temperature of the matrix [18].

5.5. Mechanical properties

The mechanical properties of the compounds are depicted in Table 3. The nanoclay filled compounds depicted better increase in overall mechanical properties. The compounds EPR/5EC and EPR/10EC showed 65 % and 97 % increase in tensile strength, 52 % and 84 % increase in tear strength respectively, compared to pure EPR. Similarly the compounds OE/5EC and OE/10EC showed 43 % and 75 % increase in tensile strength, 66 % and 125 % increase in tear strength than that of pure OE-EPDM. The enhancement in the mechanical properties is due to the better dispersion of nanoclay in the EPR and OE-EPDM matrices and rubber-filler interaction.

5.6. Scanning electron microscopy

The figure 4(a-f) showed the SEM images of the tensile fractured surfaces. The nanoclay filled compounds showed the roughness and tortuous path of the fractured surfaces (figures 4 b,c,e&f) than that of pure ones (figures 4 a&d). This may be due to the good interactions between the nanoclay and matrix polymers. The exfoliation of nanoclay platelets in the matrices may alter the crack path along their length depending on the orientation of the nanoclay layers. This may lead to higher resistance to crack propagation and thus better tensile strength was achieved.

6. Conclusion

The morphological behavior observed from XRD analysis and HR-TEM images proves the intercalation of nanoclay in ENR and further incorporation of EC in EPR and OE-EPDM matrices leads to exfoliation of the nanoclay. From curing study, faster scorch time, cure time and increase in maximum torque had been observed for the compounds containing nanoclay composites compared to that of controls. DMTA results showed better improvement in storage modulus and decrease in tan δ value accordingly upon gradual increase in nanoclay loading in both the rubber matrices, this corresponds to the higher reinforcing efficiency of the nanofiller in the matrix. The overall mechanical proper-

ties were improved for nanoclay filled compounds than that of pure ones. SEM images of fractured surfaces displayed increase in roughness and tortuous path for the nanoclay filled rubber compounds, which may be due to the better interactions between the nanoclay and rubber matrix.

References

1. Arroyo M., Lopez Manchado M.A., Herrero B. *Organo-montmorillonite as substitute of carbon black in natural rubber compounds*. *Polymer*, 2003, **44**, 2447–2453.
2. Chang Y., Yang Y., Ryu S., Nah C. *Preparation and properties of EPDM/organomontmorillonite hybrid nanocomposites*. *Polymer International*, 2002, **51**, 319–324.
3. Usuki A., Tukigase A., Kato M. *Preparation and properties of EPDM-clay hybrids*. *Polymer*, 2002, **43**, 2185–2189.
4. Duquesne S., Jama C., Le Bras M., Delobel R., Recourt P., Gloaguen J.M. *Elaboration of EVA-nanoclay systems – characterization, thermal behaviour and fire performance*. *Composites Science and Technology*, 2003, **63**, 1141–1148.
5. Arroyo M., Lopez-Manchado M.A., Valentin J.L., Carretero J. *Morphology/behavior relationship of nanocomposites based on natural rubber/epoxidized natural rubber blends*. *Composites Science and Technology*, 2007, **67**, 1330–1339.
6. Teh P.L., Mohd Ishak Z.A., Hashim A.S., Karger-Kocsis J. *Effects of epoxidized natural rubber as a compatibilizer in melt compounded natural rubber-organoclay nanocomposites*. *European Polymer Journal*, 2004, **40**, 2513–2521.
7. Varghese S., Karger-Kocsis J., Gatos K.G. *Melt compounded epoxidized natural rubber/layered silicate nanocomposites: structure-properties relationships*. *Polymer*, 2003, **44**, 3977–3983.
8. Rajasekar R., Das T., Pal K., Pal S.K., Peng Z., Chen Y., Das C.K. *Use of ENR / nanoclay composites in NR gum compounds*. *Nano Trends: A Journal of Nanotechnology and its Applications*, 2007, **3**, 1–15.
9. Rajasekar R., Pal K., Pal S.K., Peng Z., Chen Y., Das C.K. *Effect of epoxidized natural rubber-nanoclay composites in carbon black filled natural rubber vulcanizates*. *ICFAI Journal of Science & Technology*, 2008, **4**, 17-29.
10. Rajasekar R., Heinrich G., Das A., Das C.K. *Development of SBR-nanoclay composites with epoxidized natural rubber as compatibilizer*. *Research Letters in Nanotechnology*, 2009, Article ID 405153, doi:10.1155/2009/405153, 1-6.
11. Rajasekar R., Pal K., Heinrich G., Das A., Das C.K. *Development of NBR-nanoclay composites with epoxidized natural rubber as compatibilizer*. *Materials and Design*, 2009, **30**, 3839–3845.
12. Zilg C., Thomann R., Mülhaupt R., Finter J. *Polyurethane nanocomposites containing laminated*

- anisotropic nanoparticles derived from organophilic layered silicates. *Advanced Materials*, 1999, **11**, 49-52.
13. Ganter M., Gronski W., Reichert P., Mulhaupt R. Rubber nanocomposites: Morphology and mechanical properties of BR and SBR vulcanizates reinforced by organophilic layered silicates. *Rubber Chemistry and Technology*, 2001, **74**, 221-235.
 14. Zhang L.Q., Wang Y., Sui Y., Yu D. Morphology and mechanical properties of clay/styrene-butadiene rubber nanocomposites. *Journal of Applied Polymer Science* 2000, **78**, 1873-1878.
 15. Vaia R.A., Ginnelis E.P. Polymer Melt Intercalation in Organically-Modified Layered Silicates: Model Predictions and Experiment. *Macromolecules* 1997, **30**, 8000-8009.
 16. Kuila T., Srivastava S.K., Bhowmick A.K., Saxena A.K. Thermoplastic polyolefin based polymer – blend-layered double hydroxide nanocomposites. *Composites Science and Technology*, 2008, **68**, 3234–3239.
 17. Das A., Costa F.R., Wagenknecht U., Heinrich G. Nanocomposites based on chloroprene rubber: Effect of chemical nature and organic modification of nanoclay on the vulcanizate properties. *European Polymer Journal*, 2008, **44**, 3456–3465.
 18. Huang H.H., Wilkers G.L., Carlson J.G. Structure-property behaviour of hybrid materials incorporating tetraethoxysilane with multifunctional poly(tetramethylene oxide). *Polymer*, 1989, **30**, 2001-2012.

