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TPEV/Layered Silicate Nanocomposites with Dynamic Vulcanizing Process

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Thermoplastic Elastomer Vulcanizates (TPEV) prepared by dynamic vulcanizing process, is a material which has both the properties of a vulcanized rubber (elasticity) and thermoplastics (processibility). TPEV is cost effective for its good processibility and eco-friendly for its recyclability. TPEV/layered silicate nanocomposites can give a greater advantage of weight reduction which is a key issue in automotive industry because of fuel efficiency. Applying TPEV/layered silicate nanocomposites, the amount of reinforcement mineral filler can be reduced greatly compared to general TPEV which is reinforced by talc or kaolin clay. The mechanical strengths of TPEV/layered silicate nanocomposites using small amounts of MMT is similar to those of general TPEV using larger amounts of general filler. Various evaluations such as degree of crosslinking, degree of filler dispersion (XRD and TEM), surface hardness and tensile properties were carried out for the TPEV/layered silicate nanocomposites.

Keywords: TPEV, thermoplastic elastomer vulcanizates, organoclay, TPEV/layered silicate nanocomposites, dynamic vulcanization.

1 Introduction

A unique kind of thermoplastic elastomers(TPE), thermoplastic elastomer vulcanizates (TPEV) possess not only the characters of TPE which can be represented by the properties of vulcanized rubber and processibility of thermoplastics, but also advantages of chemical resistance and heat resistance provided through by chemical crosslinking in the TPEV system. Since the first commercial TPEV (polypropylene and ethylene-propylene-diene terpolymer(EPDM)) was developed by Coran(1), many kinds of TPEV were further developed and applied in various industry areas with two main advantages of total cost effectiveness in processing and recyclability (2). Recently, weight reduction has become a main issue in the automotive industry for improving fuel efficiency, since more than 60% of TPEV is used for automotive parts (3). In general, TPEV is composed of EPDM, PP, mineral oil and about 10% of talc or kaolin clay as reinforcement filler. There have been many reports on polymer/layered silicate nanocomposites (4-16), and it has been shown that nanoclay can give maximized reinforcing effect (4–7, 14–16) by using a small amount of nanoclay compared to a larger amount of conventional filler. In this study, a small amount of organified montmorillonite (MMT) nanoclay was used instead of talc or kaolin clay to reduce the density of TPEV. There have been few reports on TPEV/layered silicate nanocomposites (17-21). Most of these studies carried out using commercial TPEV, partially cured TPEV or sulfur curing system. In this study, TPEV/layered silicate nanocomposites were prepared by dynamic vulcanizing process (22–24) using a phenolic resin curing system, and the effect of the degree of dispersion of the organoclay on the properties such as the crosslinking degree, morphology and tensile properties were investigated.

2 Experimental

2.1 Materials

EPDM(KEP-960F, Mooney viscosity(ML_{1+4} at 125°C): 49, ENB Contents: 5.7 wt%, ethylene contents: 70 wt%, 50 phr oil extended, Kumho Polychem, Korea), homo polypropylene (Y-130, melt index (at 230°C, 2.16 kg loaded): 4 g/10 min, Honam Petrochemical Corp. Korea)), mineral oil (WO-1900H, kinematic viscosity (40°C): 140 cSt, aromatic oil contents : 0 wt%, naphthenic oil contents: 32 wt%, paraffinic oil contents: 68 wt%, Michang Oil Corp.,

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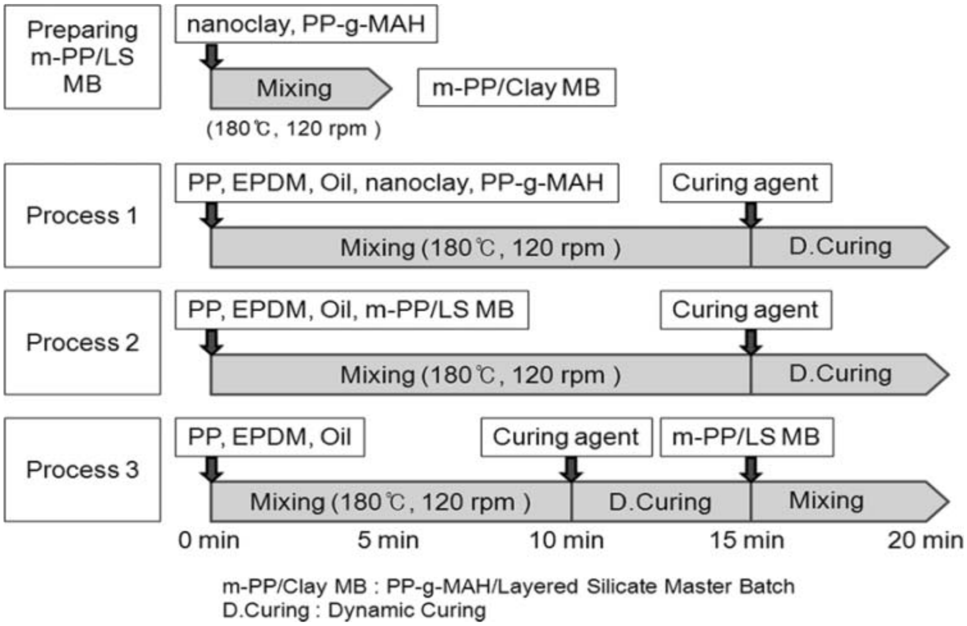


Fig. 1. Preparation schemes of TPEV/layered silicate nanocomposites.

Korea) were used as the base material of TPEV. *p*-octylphenol-formaldehyde resin (SP-1045, Schenectady, USA) was used as a curing agent. PP-g-MAH(Adpoly, MAH contents: 4%, Honam Petrochemical Corp., Korea) was used as the compatilizer. Two kinds of organoclay (Cloisite® 15A-inorganic content: 57 wt%, Cloisite® 20A-inorganic content: 62 wt%, Southern Clay Product, USA) and pristine MMT (Cloisite® Na$^+$ (Southern Clay Products, Inc., USA, CEC = 92.6meq/100 g) were used as a layered silicate. Several chemicals were used as a co-curing agent and antioxidants.

2.2 Preparations of TPEV/Layered Silicate Nanocomposites

A Brabender Plasticoder mixer (model : W350E-3zone) with counter rotating two roll blades was used for the preparation of the TPEV/layered silicate nanocomposites. The temperature of the mixer was 180°C. The blade speed was maintained at 120 rpm for 20 min. Three different processes were employed. Process 1 is that all the materials except the curing agent were added simultaneously and mixed for 15 min. After mixing, a curing agent was added to the mixer and dynamically cured for 5 min. PP-g-MAH/layered silicate master batch was used in Process 2 and 3. PP-g-MAH/layered silicate master batch is prepared by Brabender Plasticorder mixer at 180°C and 120 rpm for 5 min. In process 2, PP, EPDM, mineral oil and PP-g-MAH/layered silicate master batch were added simultaneously and mixed for 10 min. After mixing, a curing agent was added to the mixer and dynamically cured for 5 min. In process 3, PP, EPDM, mineral oil were added simultaneously and mixed for 10 min. After mixing, a curing agent was added to the mixer and dynamic cured for 5 min. After curing, PP-g-MAH/layered silicate master batch was added and mixed for 5 min. The scheme of each process is given in Figure 1.

2.3 Formulation and Notation

In all samples, fractions of oil extended EPDM, PP, mineral oil and PP-g-MAH were fixed as 52 wt%, 15 wt%, 28 wt% and 5 wt%, respectively. The fraction of pure EPDM was 34.7 wt% and the fraction of total oil was 45.3%. This basic formulation corresponds to the conventional TPEV formulation which shows surface hardness of Shore A 70 using 12 phr of mineral filler. A controlled amount of each filler and curing agent was added into the above basic formulation. In this research, all samples were designed for preparing the fully cured TPEV which has 100% of crosslinking density.

The code for TPEV/layered silicate nanocomposites was arranged as follows:

$$(k)\text{-}(l)\text{-X}(m)\text{P}(n)$$

In the first variable group, $(k)(l)$, 'k' represents the type of filler and 'l' the contents of filler. The third variable 'm' indicates the contents of curing agent. The last variable 'n' represents the preparation process. Each notation is summarized in Table 1.

Table 1. Notation of TPEV/layered Silicate Nanocomposites

k Kind of Filler		*l* Contents of Filler		*m* Contents of Curing Agent		*n* Used Process	
Code	*Meaning*	*Variable*	*Meaning*	*Variable*	*Meaning*	*Code*	*Meaning*
C0	No filler						
T	Talc						
CK	Kaolin Clay	1	1 wt%	1	1 wt%	1	Process 1
CNa	Cloisite® Na^+	3	3 wt%	2	2 wt%	2	Process 2
C15	Cloisite® 15A	5	5 wt%	3	3 wt%	3	Process 3
C20	Cloisite® 20A						

2.4 Evaluation of Density

Densities of all samples were measured by the auto-densimeter (Mirage, Electronic Densimeter, SD-120L, Japan) corresponding to ASTM D792.

2.5 Evaluation of Crosslinking Degree

Crosslinking degree is one of the most important parameters in TPEV materials since most of the properties depend on crosslinking degree. Crosslinking degree is defined as the fraction of crosslinked EPDM in total EPDM and evaluated by measuring the insoluble contents in boiling xylene for 16 h. PP, non-cross-linked EPDM and oil could be dissolved in boiling xylene, but filler and crosslinked EPDM could not be dissolved in boiling xylene. The amount of crosslinked EPDM can be calculated by subtracting the filler content from the filtered residue.

2.6 Morphology Characterization

TEM specimens were prepared by using a microtome (Leica, Ultracut UCT, Austria) with a cryogenic EMFCS system. The specimens were cut with a diamond knife at -120°C. TEM micrographs were obtained by using a field emission transmission electron microscopy(FEI Company, Tecni G2 F30, USA). Wide-angle X-ray diffraction was obtained at ambient temperature on X-ray diffractometer (Rigaku, D/MAX-2200V, Japan) with CuK radiation to determine the d-spacing of the organoclay. Each sample was scanned from $2\theta = 0.6^\circ$ to 10° at a scan rate of 0.5°/min.

2.7 Evaluation of Surface Hardness

Evaluations of surface hardness were carried out with the Shore A Durometer (Zwick, Germany) according to ASTM D2240 with specimens of 6 mm thickness.

2.8 Evaluation of Tensile Properties

Tensile tests were carried out with the Universal Tensile Tester (Instron 5566, USA) according to ASTM D412. The grip distance of 25 mm was used and the crosshead speed was 500 mm/min.

3 Results and Discussion

3.1 Crosslinking Degree

In Figure 2, crosslinking degree changes with different types of filler in process 1 were given. Although all samples were designed for fully cured TPEV, nanocomposites with Cloisite® 15A and Cloisite® 20A show a large decrease in the crosslinking degree as the amount of filler increased. Similar behavior was observed in process 2, although the decrease in the crosslinking degree was somewhat low. In process 3, adding organoclay master batch after curing prevented the decrease in crosslinking degree and showed fully cured TPEV (Figure 3). From these phenomena, we can presume that dimethyl dehydrogenated tallow having quarternary ammonium cation as the organifier in the organoclay retarded crosslinking reaction between 5-Ethylidene-2-Norbornene in EPDM and p-octylphenol formaldehyde resin as curing agent. The retarding effect was very serious. Even through increments of a curing agent

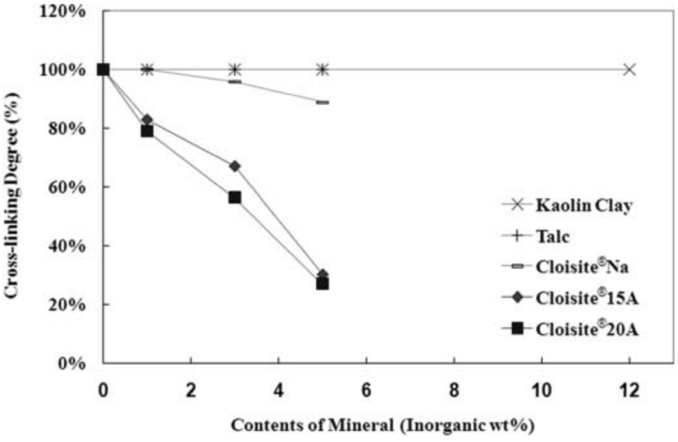


Fig. 2. Crosslinking degree of nanocomposites prepared by process 1 as a function of mineral contents.

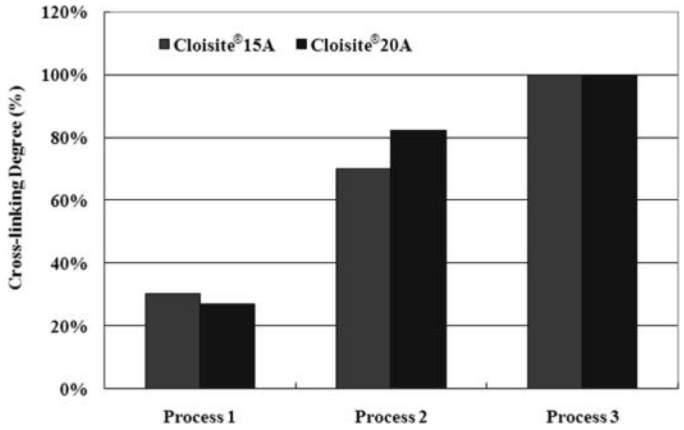


Fig. 3. Crosslinking degree of nanocomposites prepared by process 1, process 2 and process 3 (content of organoclay: 5%).

by 2 or 3 times, fully cured TPEV could not obtained easily as seen in Figure 4.

3.2 Degree of Dispersion of Organoclay

Figures 5 and 6 shows the XRD patterns for TPEV/layered silicate nanocomposites using Cloisite® 15A and Cloisite® 20A, respectively. In all samples, the d-spacing increased from 1.2 to 2 times to that of the organoclay.

Figure 5(a) shows the effect of the organoclay content when the nanocomposites were prepared by process 3. Cloisite® 15A shows d-spacing of 2.94 nm and the d-spacing increased to 3.07 nm in PP-g-MAH/organoclay master batch. The d-spacing of Cloisite® 15A increased further when the nanocomposites were prepared. The d-spacing of 4.44 nm was observed in 1% organoclay content and the d-spacing decreased to 3.59 nm in 3% organoclay content. The nanocomposites with 1% organoclay shows better dispersion compared to nanocomposites with 3% organoclay.

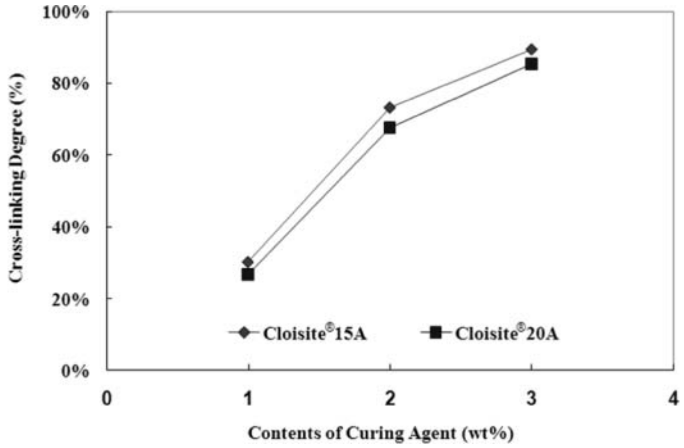


Fig. 4. Crosslinking degree of nanocomposites as a function of contents of curing agent prepared by process 1 (content of organoclay: 5%).

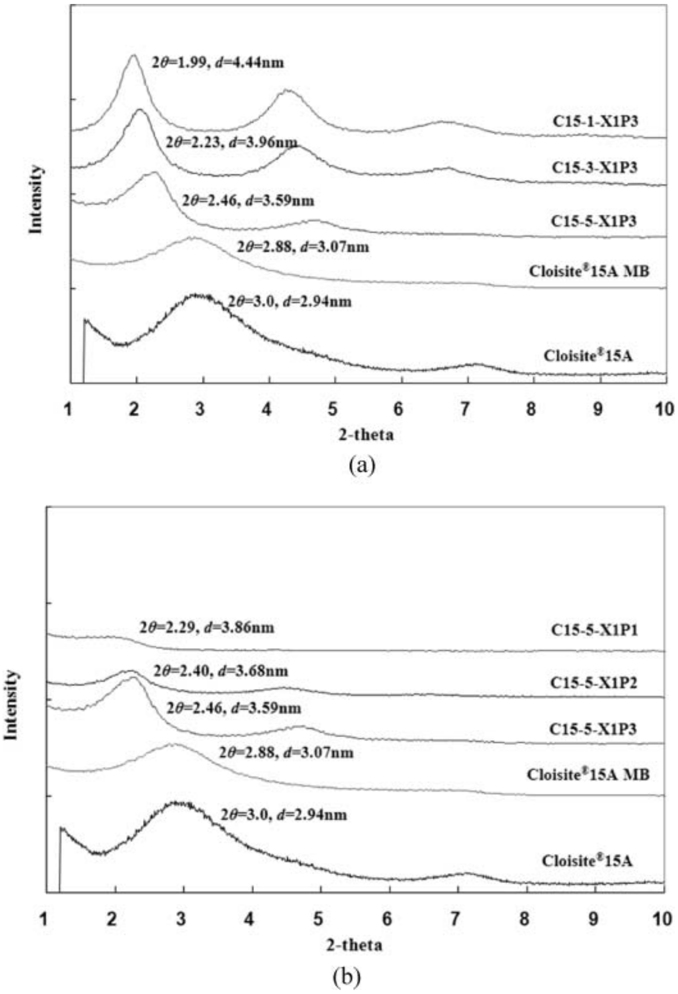


Fig. 5. XRD patterns of TPEV/layered silicate nanocomposites with Cloisite® 15A (a) effect of organoclay content, (b) comparing preparation process.

Figure 5(b) shows the effect of different mixing sequence. Process 1 shows the largest d-spacing of 3.86 nm while process 3 shows d-spacing of 3.07 nm with 5% organoclay content. A similar trend was observed in nanocomposites with Cloisite® 20A (Figure 6) Nanocomposites with Cloisite® 20A showed better dispersion when compared to nanocpmposites with Cloisite® 15A. C20-1-X1P3, nanocomposite with 1% Cloisite® 20A in process 3 shows d-spacing of 4.82 nm while the corresponding nanocomposite C15-1-XP3 shows 4.44 nm d-spacing. In terms of the degree of dispersion, nanocomposites having 1% Cloisite® 20A shows the best dispersion.

In Figures 7 and 8, TEM images of each process having 5% of organoclay are shown. In process 1, organoclays are located in the whole region of cross-linked EPDM and PP

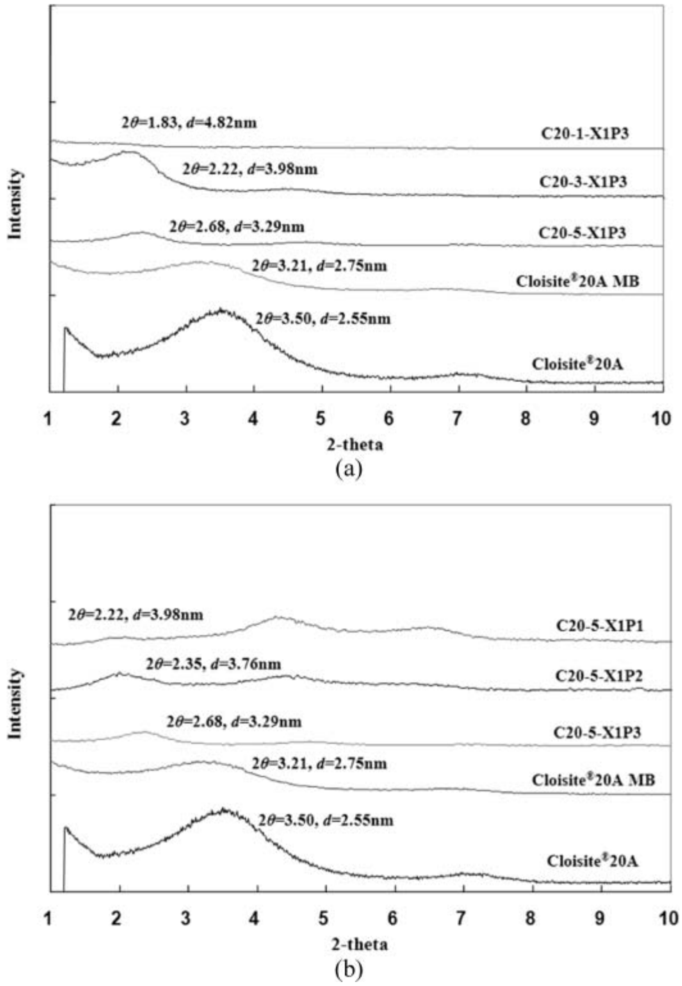


Fig. 6. XRD patterns of TPEV/layered silicate nanocomposites with Cloisite® 20A (a) effect of organoclay content, (b) comparing preparation process.

phase. In process 2, organoclay are in PP phase mainly but rarely in EPDM phase. In process 3, organoclay can be found in only PP phase.

3.3 Surface Hardness and Tensile Strength

Surface hardness and tensile strength of TPEV/layered silicate nanocomposites with process 1 are shown in Figures 9 and 10, and those with process 3 are shown in Figures 11 and 12. Surface hardness and tensile strength depend on the degree of cross-linking. In nanocomposites filled with kaolin clay or talc, surface hardness and tensile strength increased increasing mineral content. But in cases of using organoclay, surface hardness and tensile strength significantly decreased with increasing organoclay content since the organifier present in the organoclay somehow retarded the curing reaction. In process 3, when the organoclays are introduced after the curing reaction, surface hardness and tensile strength increase with increasing organoclay contents. Tensile strength of C15-3-X1P3 is 6.5 MPa which is equivalent to CK-12-X1P1, conventional TPEV which has Shore A 70 of surface hardness and 6.5 MPa of tensile strength using 12 wt% of kaolin clay. It means that only 3 wt% of well intercalated organoclay can improve tensile properties of the composite to a level using 12 wt% of general mineral as the reinforcing filler. Surface hardness of C15-3-X1P3 in shore A is 74, it is higher than CK-12-X1P1 for about 6%. The main reason of higher surface hardness is presumed that intercalated organoclay existed only in PP matrix in C15-3-X1P3. In

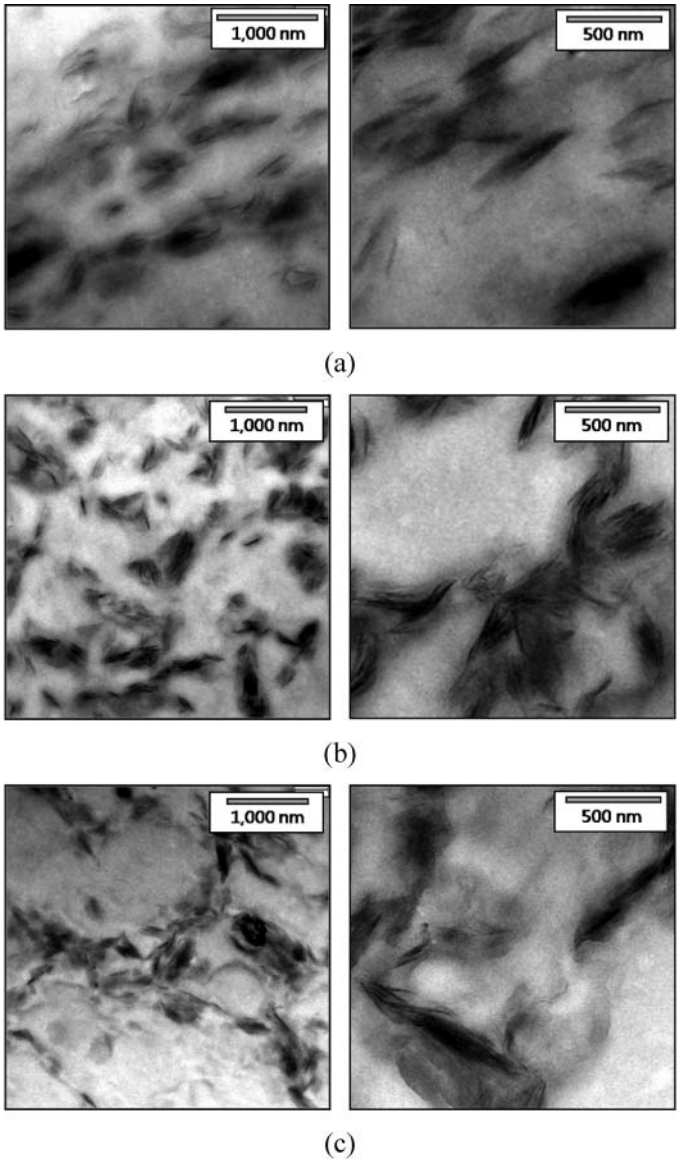
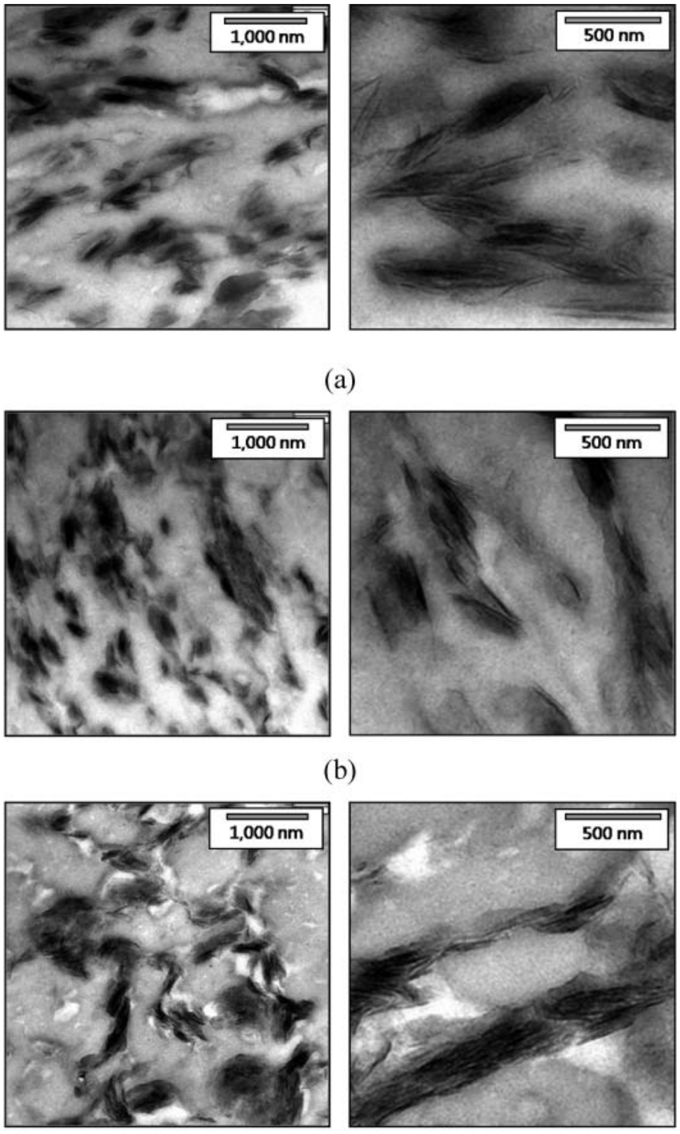


Fig. 7. TEM micrographs of TPEV/layered silicate nanocomposites with Cloisite® 15A prepared by process 1, process 2 and process 3 (content of organoclay: 5%) (a) C15-5-X1P1, (b) C15-5-X1P2, (c) C15-5-X1P3.



(a)

(b)

(c)

Fig. 8. TEM micrographs of TPEV/layered silicate nanocomposites with Cloisite® 20A prepared by process 1, process 2 and process 3 (content of organoclay: 5%) (a) C20-5-X1P1, (b) C20-5-X1P2, (c) C20-5-X1P3.

terms of tensile strength, Cloisite® 15A was better than Cloisite® 20A.

3.4 Density

Densities of nanocomposites increase with contents of mineral linearly as seen in Figure 13. The density of C-0-X1P1, not filled sample, is 0.887 g/ml, but CK-12-X1P1, conventional TPEV with 70 Shore A hardness is 0.97 g/ml. The density of C15-3-X1P3 which is equivalent to CK-12-X1P1 is 0.91 g/ml which is lighter by about 6% (Fig. 14).

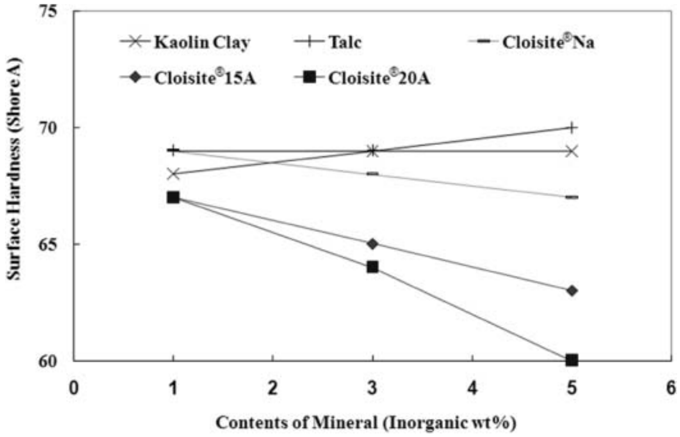


Fig. 9. Surface hardness as a function of mineral contents comparing nanocomposites with kaolin clay, talc, Cloisite® Na, Cloisite® 15A and Cloisite® 20A prepared by process 1.

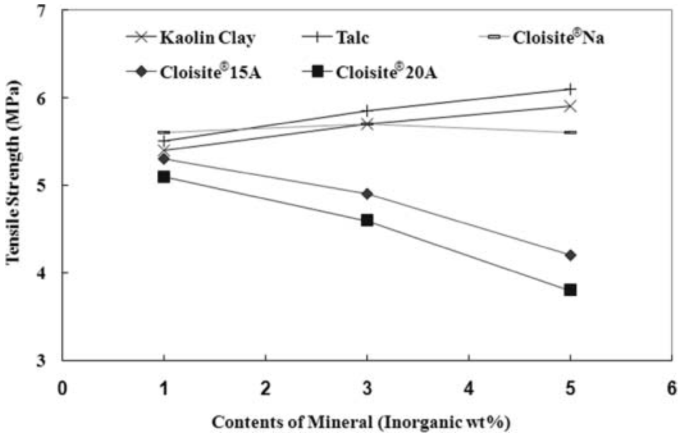


Fig. 10. Tensile strength as a function of mineral contents comparing nanocomposites with kaolin clay, talc, Cloisite® Na, Cloisite® 15A and Cloisite® 20A prepared by process 1.

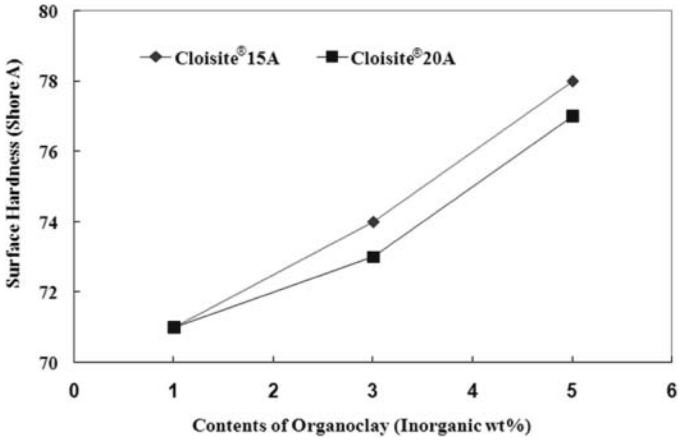


Fig. 11. Surface hardness as a function of organoclay contents comparing nanocomposites with Cloisite® 15A and Cloisite® 20A prepared by process 3.

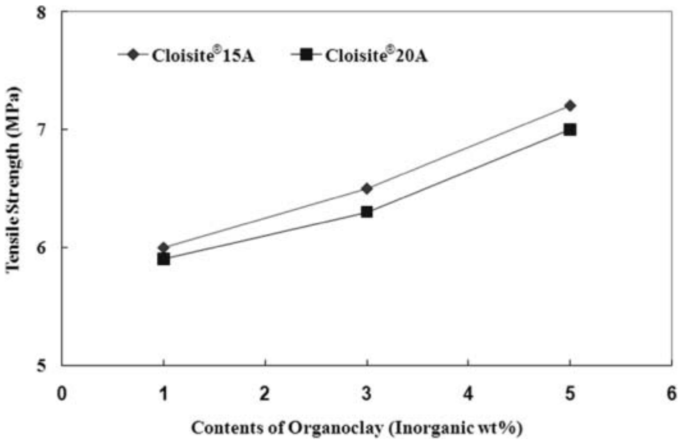


Fig. 12. Tensile strength as a function of organoclay contents comparing nanocomposites with Cloisite® 15A and Cloisite® 20A prepared by process 3.

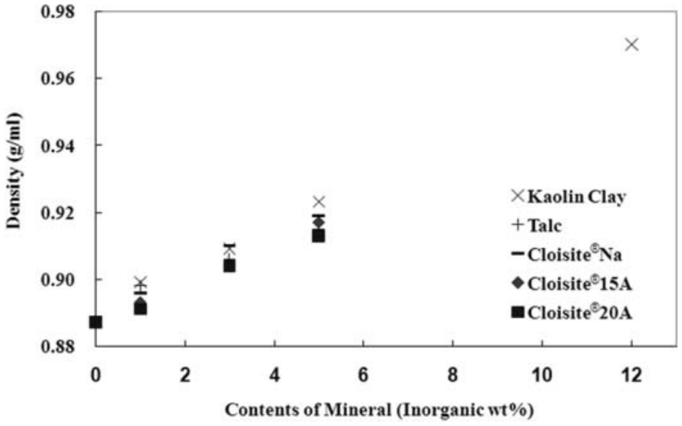


Fig. 13. Density as a function of mineral contents comparing nanocomposites with kaolin clay, talc, Cloisite® Na, Cloisite® 15A and Cloisite® 20A prepared by process 1.

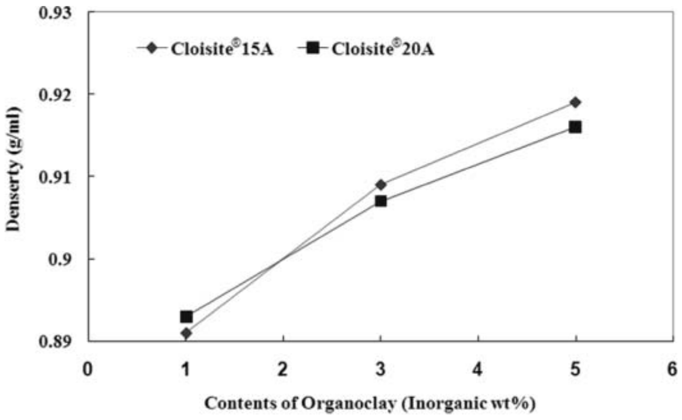


Fig. 14. Density as a function of organoclay contents comparing nanocomposites with Cloisite® 15A and Cloisite® 20A prepared by process 3.

4 Conclusions

In this study, TPEV/layered silicate nanocomposites using organoclay with 3 different processes were prepared. The crosslinking degree, morphology, surface hardness, tensile properties and densities of the TPEV/layered silicate nanocomposites were investigated. It was found that the organifier in the organoclay retarded the cross-linking reaction between the diene in EPDM and the curing agent. Fully cured TPEV/layered silicate nanocomposites were successfully obtained using process 3 when the organoclay/PP-g-MAH was fed after the crosslinking reaction was completed.

The degree of dispersion of organoclays in nanocomposites prepared by three different processes was investigated by XRD and TEM. In all nanocomposites, the d-spacing increased from that of the organoclay. Nanocomposites with Cloisite® 20A showed somewhat bigger d-spacing compared to nanocomposites with Cloisite® 15A The nanocomposites with 1% organoclay shows better dispersion compared to nanocomposites with 3% organoclay. Three different processes to prepare the nanocomposite resulted in morphology showing different location of the silicate. In process 1, organoclay could be found in the whole region of the nanocomposite, but in process 3, organoclay can be found only in PP phase. The d-spacing of the silicate layers in nanocomposites prepared by process 1 was bigger than process 2 and process 3.

The d-spacing of silicate layers varied from 4.82 nm to 3.29 nm. C20-1-X1P3 nanocomposites filled with 1% Cloisite® 20A prepared by Process 3 showed the largest d-spacing of 4.82 nm.

The surface hardness and the tensile strength significantly depended on the crosslinking degree. In the fully cured TPEV/layered silicate nanocomposites, the surface hardness and the tensile strength significantly increased with increasing the clay content. In terms of mechanical strength, the TPEV/layered silicate nanocomposites (C15-3-X1P3) which was equivalent to general TPEV showed higher surface hardness and lower density.

Acknowledgments

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