Study on the structure and properties of RTV/FR-DOMt nanocomposites

Wei Xiaofeng, Wang Jincheng and Zhao Yi

Department of Polymeric Materials and Engineering, College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, P.R. China

ABSTRACT

The aim of our research was to study the effect of flame-retardant dendrimer modified organic montmorillonite (FR-DOMt) with different ratios on the structure and properties of room-temperature-vulcanised silicone rubber (RTV). The physical and mechanical properties of RTV nanocomposites were improved with the addition of FR-DOMt additives. The RTV nanocomposites exhibited better thermal stability. $T_{onset}$ of RTV/FR-DOMt-3 was 310 °C, 100 °C higher than that of pure RTV. RTV/FR-DOMt-3 nanocomposite possessed the highest elongation at break, 500%. This was 46% higher than that of pure RTV. In addition, these RTV nanocomposites showed an increased FR behavior. By adding 3–15 phr of FR-DOMt into pure RTV matrix, a linear decrease of burning rate together with an increase of LOI values were obtained. SEM and TEM observations of RTV/FR-DOMt-3 demonstrated that the exfoliated silicate layers dispersed uniformly in this nanocomposite.

1. Introduction

Room-temperature-vulcanised silicone rubber (RTV) is a type of high-temperature-resistant synthetic rubber. It possesses low-temperature toughness, electrical-insulating and high thermal stability. RTV has now been widely used in many fields such as electronic and electric industries.[1–3] In these industries, the flame-retardant (FR) materials are strongly required. However, RTV may burn constantly when it is ignited. Thus, research on RTV with better FR ability is needed.

Combinations of inorganic functional fillers and polymeric materials are used to solve the above major shortcomings of RTV.[4] One of the promising inorganic fillers in this field is montmorillonite (Mt). The structural unit of Mt is two tetrahedral sheets. These sheets sandwich a central octahedral sheet. The silicate layers are about 10 Å in thickness and 1000–2000 Å in length and width. Numerous studies were focused on this clay due to its high cation exchange capacity, swelling capacity and strong adsorption capacities.[5,6] However, the hydrophilic surface nature of Mt may hinder its uniform dispersion in the organic polymer matrix. Conventional cationic surfactants exchange is one of the
main methods for the surface modification of Mt. However, this method is not beneficial for the obvious increase of its interlayer space, and sometimes may reduce its thermal stability.[7,8] Thus, FR and other mechanical performance of RTV cannot be significantly improved by the addition of this type of organoclay.

Due to the plenty of functional end groups, three-dimensional networks and high compatibility with other polymers, a novel type of macromolecule, dendrimer, has received more attention.[9] Dendrimer possesses special characteristics of both molecular chemistry and polymer chemistry. Their step-by-step controlled synthesis belongs to molecular chemistry, while monomer—polymer behaviour is owned by polymer chemistry.[10,11] In our previous work, a novel type of FR dendrimer modified organoclay, FR-DOMt, was prepared and characterised.[12] Results revealed that the use of dendrimers can increase the interlayer spacing and thermal stability of organic montmorillonite (OMt). In addition, this dendrimer contained phosphorus, nitrogen and boron elements. Thus, FR ability of these elements in FR-DOMt can be used to prepare a new type of enhanced polymer.

In the present work, RTV/FR-DOMt nanocomposites were fabricated using this novel type of organoclay. The properties such as tensile strength, elongation at break, thermal stability and flame-retardance were researched and compared. As a result, these RTV nanocomposites exhibited better thermal stability, tensile properties and FR behaviour.

2. Experimental

2.1. Materials

RTV, two components (A:B, 1:1, 30% aerosilica, component A: hydrogenous silicane, Si-(O-Si-(CH₃)₂-H)₄; component B: ethylene-terminated polysiloxane, CH₂ = CH-Si(CH₃)₂ O(Si(CH₃)₂O)ₙ-Si(CH₃)₂-CH = CH₂, and the organic platinum catalyst), industrial grade, were supplied by Bluestar Silicones Shanghai Company (Shanghai, China). Na⁺-Mt, denoted as Mt, industrial grade, was obtained from Zhejiang Fenghong Clay Company (China). FR-DOMt were prepared by us.[12]

2.2. Preparation of RTV nanocomposites

A certain amount of FR-DOMt, for example, 0, 3, 5, 10, 15 phr, was mixed with 10 g hydrogenous silicane, one component of RTV. Then, this mixture was vigorously stirred at room temperature for 3 h. After that, the mixture was blended with 10 g ethylene-terminated polysiloxane, the other component of RTV, and stirred for 2 min. Last, the mixture was poured into a Teflon mould. Elastic films were obtained after curing at room temperature 20 °C for 24 h. To compare and reveal the FR and reinforcing abilities of this novel organoclay in RTV, Mt was added into RTV matrix, and RTV/Mt nanocomposites were prepared.

2.3. Characterisation

Thermogravimetric analysis (TGA) was performed at 10 °C/min under air using a Linseis PT-1000 equipment. The flow rate was 5 × 10⁻⁷ m³/s. The mass of the samples was fixed at 10 mg. The precision of the temperature measurements was 1 °C.
Differential scanning calorimetry (DSC) measurements were made on a Linseis PT-10 equipment. To investigate their glass transition temperatures, the samples were heated from $-50^\circ\text{C}$ to $10^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$.

Horizontal burning behaviour was evaluated on a horizontal and vertical burning tester (5400, Kunshan) according to ASTM D635. The size of the samples was $(125 \pm 5 \text{ mm}) \times (13.0 \pm 0.5 \text{ mm}) \times 3.0(0.0 \pm 0.2\text{mm})$. Limiting oxygen index (LOI) was tested using a Stanton Redcroft instrument on sheets with a size of $100 \times 10 \times 3 \text{ mm}^3$ according to ASTM 2863.

Tensile test was carried out on a TCR-2000 instrument at room temperature with a crosshead speed of 500 mm/min. Samples with a standard dumbbell shape were manufactured. Medium data were obtained after five times of repeating measurements. Their hardness was measured by an XY-1 Shore durometer.

X-ray diffraction (XRD) was taken at room temperature with a Rigaku D-Max/400 diffractometer. The X-ray beam was nickel-filtered Cuk$_\alpha$ ($\lambda = 0.154$ nm) radiation. It worked at 50 $\text{kV}$ and 150 $\text{mA}$. The data were obtained from $1^\circ$ to $10^\circ$ ($2\theta$) at a rate of $2^\circ/\text{min}$.

Scanning electron microscopy (SEM) was observed using a Hitachi S-2150 instrument. The samples were gold-coated with an IB-3 ionic sputtermeter.

Transmission electron microscopy (TEM) was done using a JEM-2010 instrument. The acceleration voltage used was 80 $\text{kV}$. The ultra-thin films were prepared by cryo-ultramicrotomy and sliced with a microtome into $80-100 \text{ nm}$ thickness at $-100^\circ\text{C}$.

3. Results and discussion

3.1. The effect of dendrimer on structure and properties of FR-DOMt

The FR-DOMt additive we used in the preparation of RTV nanocomposites was synthesised by tetrahydroxymethyl phosphonium chloride (THPC), N, N-dihydroxyl-3-amino-methyl propionate and boric acid.

Mt was first modified by THPC, and a type of organoclay, OMt, was obtained. Three generations of dendrimer modified organic clay minerals, DOMt-1, DOMt-2 and DOMt-3, were successfully prepared by OMt and the monomer prepared. These DOMts were terminated by boric acid, and an FR dendrimer modified organoclay, FR-DOMt, was successfully prepared.[12] Experiments revealed that this FR-DOMt possessed better thermal stability and larger $d$-value due to steric hindering and thermal stability of the dendritic surfactant. Compared with that of Mt, the thermal stability of FR-DOMt was improved in the temperature range $30-300^\circ\text{C}$ (Figure 1(a)). The interlayer spacing was increased from 1.40 to 2.08 nm for FR-DOMt (Figure 1(b)). This was related to the bilayer to pseudo trilayer arrangement of intercalated surfactants in the interlayer spacing of FR-DOMt.

3.2. The effect of FR-DOMt on thermal properties of RTV nanocomposites

Figure 2 presented TGA and derivative thermogravimetric (DTG) curves of different RTV nanocomposites. To compare their thermal stabilities, three parameters were used, that is, the onset temperature of thermal degradation ($T_{\text{onset}}$, the temperature at which weight
loss is 5 mass%), the centre temperature of thermal degradation ($T_{\text{max}}$, the temperature at which weight loss is the fastest), and the yield of charred residue at 700 °C.[13] These data were all measured from TGA and DTG curves. They were summarised in Table 1. Overall, the thermal stability of most RTV nanocomposites was better than that of pure RTV. $T_{\text{onset}}$ of RTV/FR-DOMt-3 exhibited the highest value, 310 °C. This was 100 °C higher than that of pure RTV. However, $T_{\text{onset}}$ of other nanocomposites was decreased when more amount of FR-DOMt was added. Yuan et al. [14] also found that silicone rubber composites containing organoclay degraded slightly faster than pure silicone. As a

Figure 1. Characterisation of Mt and FR-DOMt: (a) TGA and (b) XRD.
result, a slight weight loss was found in their composites. Zhao et al. [15] ascribed the decreased initial temperature to the damaged structure resulting from the aggregated silicate layers in the polymeric composites. Here, the decreased initial degradation temperature may be resulted from the porous structure with the addition of excessive additives. More oxygen molecules existed in the holes, and this may facilitate the degradation of macromolecular chains. In addition, the intensity of the degradation peaks of RTV/FR-DOMt nanocomposites was decreased though their decomposition temperatures were not changed obviously. Thus, the thermal stability of these nanocomposites was improved.

Figure 2. Thermal stability of different RTV nanocomposites: (a) TGA and (b) DTG.
due to their high initial decomposition temperature and decreased degradation degree of decomposition peaks.[16] This was mainly attributed to good gas barrier effect and thermal stability of FR-DOMt. The layered silicates in FR-DOMt may hinder both evaporation of decomposition products and access of oxygen to the RTV matrix. In addition, the amount of volatile and small products was reduced resulting from FR ability of phosphorus, nitrogen and silicon elements in FR-DOMt which may decrease the rate of polymer chain scission.[17] It was well known that silicone rubber decomposed mainly from chain ends. This belonged to random degradation mechanism.[18–21] Moreover, the degree of random degradation was increased with the increase of temperatures.

Figure 3 showed DSC curves of different RTV nanocomposites. A transition of pure RTV existed at $-37.5 \, ^\circ C$, and this was related to its glass transition temperature ($T_g$). With the addition of FR-DOMt, $T_g$ of RTV nanocomposites was decreased to $-42.5–39^\circ C$. The decrease was about $1.5–5^\circ C$. This phenomenon was ascribed to the introduction of layered silicates and dendrimers in RTV matrix. Thus, free volume and incomplete curing reaction may occur in these nanocomposites. However, $T_g$ of these nanocomposites exhibited a trend of increase when more FR-DOMt were added. This could be due to at least the following two reasons. First, the nano-reinforcement effect of FR-DOMt in RTV matrix may give an increase in $T_g$. The nano-type of layered silicates in FR-DOMt dispersed uniformly in RTV and restricted the motion of the polymer chains. Second, the dendrimers may be entangled with the polymer chains, and this may also give rise to $T_g$.[22,23] Zhang et al. [24] attributed the increase or decrease of $T_g$ to the two

### Table 1. TGA results of different RTV nanocomposites.

|                     | $T_{\text{onset}}/^\circ C$ | $T_{\text{max}}/^\circ C$ | Residual mass/% |
|---------------------|----------------------------|---------------------------|-----------------|
| RTV                 | 210                        | 551                       | 53.3            |
| RTV/FR-DOMt-3       | 310                        | 549                       | 45.1            |
| RTV/FR-DOMt-5       | 230                        | 550                       | 43.2            |
| RTV/FR-DOMt-10      | 220                        | 552                       | 42.6            |
| RTV/FR-DOMt-15      | 130                        | 553                       | 42.1            |

![Figure 3](image-url). DSC curves of different RTV nanocomposites.
distinct interactions between rubber matrix chains. They described the surfactants of
organoclay as the ‘hooks’: one is ‘external hook’ to connect the outer surface of exfoliated
silicate layers, and the other is ‘inner one’ to interact with the internal surface of the nano-
clay. The different degree of above two interactions may cause the increase or decrease of
$T_g$.

3.3. The effect of FR-DOMt on flame-retardancy of RTV nanocomposites

The horizontal burning rate and LOI values of RTV/FR-DOMt and RTV/Mt nanocompo-
sites were compared in Figure 4. These nanocomposites showed a same combustion and
FR trend but with a different degree. They presented a linear decrease of burning rate due
to the flame inhibition effect of Mt and FR-DOMt. By adding 15 phr of FR-DOMt into
pure RTV, the burning rate of the nanocomposite was 0.041 mm/s. This was much slower
compared with that of pure RTV, 0.057 mm/s. Moreover, the LOI value of pure RTV was
22.0%. This meant that the pure RTV was almost flammable in an air environment. By
adding 15 phr of FR-DOMt into RTV, the LOI value was increased to 28.0%. They
showed better fire protection. However, after loading different amounts of Mt, these RTV
nanocomposites showed decreased FR properties. The LOI value of RTV/Mt-15 was 25%,
which was lower compared with that of RTV/FR-DOMt-15.

Here, the present study described the application of dendrimer modified organoclay,
FR-DOMt, in RTV matrix. This novel additive was composed of dendrimer and layered
silicates. The dendrimer contained phosphorus, nitrogen and boron elements. It behaved
like a surfactant for surface modification of Mt. In addition, the layered silicates owned sil-
icone element. The FR and smoke inhibition effects of phosphorus, nitrogen, boron and
silicon elements in this organoclay can be used to fabricate an enhanced FR type of clay
nanocomposites. Regarding the improvement of FR performance in RTV nanocompo-
sites, FR-DOMt in the polymer matrix may have the following FR mechanism. First, an
excellent barrier effect may be formed resulting from the silicate layers of organoclay.
They may migrate towards the surface of the matrix and become a physical barrier. Dur-
ing combustion, flammable molecules were produced from the degradation of polymer
chains. These small molecules were slowed down and obstructed to move to the combus-
tion interface. Second, aromatic compounds may develop from the degradation process.
These products may come from the complex reactions between phosphorus, nitrogen and
boron elements in the dendrimer. Third, carbonaceous layers may be produced from the
degradation products of RTV and methylene groups in the dendrimer. They can serve as
another physical barrier. The outside oxygen penetrating into the internal matrix may be
slowed down by these charred layers. Thus, the combustion at the interface of RTV may
be inhibited or delayed.[25] The scheme of FR mechanism in these RTV nanocomposites
was given in Scheme 1.

3.4. The effect of FR-DOMt on tensile properties of RTV nanocomposites

Figure 5 depicted and compared the effect of FR-DOMt and Mt on tensile properties of
RTV nanocomposites. These two types of nanocomposites showed different trends in their
tensile properties. The FR-DOMt reinforced RTV exhibited decreased tensile strength and
some improved elongation at break. The RTV/FR-DOMt nanocomposite possessed the
highest elongation at break, 500%, at loading of 3 phr of FR-DOMt. This was 46% higher than that of pure RTV. However, the tensile strength of RTV/FR-DOMt-3 was decreased to 3.1 MPa. This was a little lower compared with that of pure RTV, 3.4 MPa. The improvement of the elongation at break may be attributed to the following three reasons: (1) the delocalised and absorbed stress due to the uniform dispersion of silicate layers in RTV matrix; (2) the enhanced slipping of the clay tactoids due to the ‘external hook’ effect of the dendrimer; (3) the plasticising effect of the dendrimer in RTV matrix.[26] The

Figure 4. FR behaviour of different RTV nanocomposites: (a) burning rate, (b) LOI.
toughening mechanism of FR-DOMt in RTV was illustrated in Scheme 2. As to the nanocomposites with different amounts of Mt, they showed another trend. After loading 3 phr of Mt, the tensile strength and elongation at break of the nanocomposite was increased to the highest value, 3.8 MPa and 420%. This phenomenon was ascribed to the reinforcing and toughening ability of the nanoclay. In addition, the tensile properties of these RTV nanocomposites were decreased with the addition of more FR-DOMt and Mt. Owing to clay aggregates were formed in the matrix, the interfacial area between the polymer and the layered silicates may be reduced. This interaction may cause stress concentrating and resultant decreasing strength. [14,27]

The hardness of the two types of RTV nanocomposites showed opposite trends. The hardness of RTV/FR-DOMt nanocomposites was almost decreased when more FR-DOMt was added (Figure 6). FR-DOMt was composed of nanoclay and dendrimer. The nanoclay was a kind of inorganic material and owned high hardness, while the dendrimer with no crosslinking had a low value. The above result illustrated that the nanoclay and dendrimer in FR-DOMt can affect the hardness of RTV matrix, respectively. However, RTV/Mt nanocomposites showed an obviously increased trend. This increase of hardness was mainly resulted from the increased amount of the inorganic nanoclay with high hardness.

### 3.5. The effect of FR-DOMt on microstructure of RTV nanocomposites

Figure 7 showed XRD patterns of different RTV nanocomposites. The addition of FR-DOMt in RTV matrix affected its crosslinking degree and crystal size. In Figure 7(a), pure RTV exhibited one diffraction peak at $2\theta = 12.2^\circ$ (011). Although the position of the diffraction peaks of these nanocomposites showed no shift, the intensity of the peaks was changed with increasing amount of FR-DOMt. Broad halos were shown in these XRD curves, and this represented the highly amorphous nature of these RTV nanocomposites. Moreover, pure RTV showed sharper peaks compared with that of RTV nanocomposites. This observation illustrated that the pure RTV possessed more crystalline in its matrix. Due to fewer crosslinking networks existed in the pure RTV, the molecular chains had more space to align and rearrange into crystalline domains. This may give sharper peaks.
in XRD. However, chain flexibility was inhibited to a certain degree by more molecular networks in RTV nanocomposites. This may restrict any possible chain alignment to form crystalline domains.[28,29] In curves of RTV/FR-DOMt-3, 5, and 10, the basal peak of FR-DOMt at $2\theta = 4.1^\circ$ ($d = 2.08$ nm) disappeared. This illustrated that FR-DOMt was exfoliated in RTV matrix (Figure 7(b)–(d)). [30] When 15 phr of FR-DOMt were incorporated, a slight peak appeared at $2\theta = 4.1^\circ$ (Figure 7(e)). This peak was related to the $d$-spacing of FR-DOMt and illustrated that aggregated silicate layers appeared in this nanocomposite.

**Figure 5.** Tensile properties of different RTV nanocomposites: (a) tensile strength, (b) elongation at break.
To further explain the phenomenon observed from XRD curves, SEM and TEM observations were used to analyse the morphology of RTV nanocomposites.

SEM micrographs of RTV/FR-DOMt-3 were given in Figure 8. It was observed from Figure 8(a) that rubber additives, such as aerosilica, dispersed in the RTV matrix, and holes and agglomerates were formed. Compared with pure RTV, RTV/FR-DOMt-3 showed almost continuous and regular layered structure (Figure 8(b)). The various

Scheme 2. Toughening mechanism of RTV nanocomposites.

To further explain the phenomenon observed from XRD curves, SEM and TEM observations were used to analyse the morphology of RTV nanocomposites.

SEM micrographs of RTV/FR-DOMt-3 were given in Figure 8. It was observed from Figure 8(a) that rubber additives, such as aerosilica, dispersed in the RTV matrix, and holes and agglomerates were formed. Compared with pure RTV, RTV/FR-DOMt-3 showed almost continuous and regular layered structure (Figure 8(b)). The various

Figure 6. Hardness of different RTV nanocomposites.
Figure 7. XRD curves of (a) RTV, (b) RTV/FR-DOMt-3, (c) RTV/FR-DOMt-5, (d) RTV/FR-DOMt-10 and (e) RTV/FR-DOMt-15.

Figure 8. SEM images of (a) RTV, (b) RTV/FR-DOMt-3.
micron-sized and spherical domains (bright part) were also observed. These domains were likely to be clusters of FR-DOMt, aerosilica and their aggregates. Meanwhile, the molecular chains arrangement of dendrimer inside the clay galleries of FR-DOMt could contribute to the morphologies of the nanocomposite. In addition, the lubricating effect of dendrimers in FR-DOMt may also influence the dispersion status of the organoclay in RTV nanocomposite. As a consequence, addition of FR-DOMt into pure RTV may improve the compatibility between the macromolecules and this organoclay. Thus, the dispersion degree of the organoclay in the polymeric matrix may be promoted.

TEM micrographs of RTV/FR-DOMt-3 were presented in Figure 9. From Figure 9(a), the silicate layers did not fill the full volume, and this illustrated that the primary particles of FR-DOMt dispersed almost uniformly in RTV matrix. A careful analysis of this image showed that the morphology belonged to the sponge-like structure. This structure was composed of concentrated and less concentrated regions. The concentrated regions were formed by clay tactoids connected between each other. Moreover, the less concentrated regions were constituted by randomly oriented thin layers. From Figure 9(b), the morphology could be considered as a mixture of intercalated and exfoliated platelets. That is, molecular chains of RTV diffused between the silicate layers of FR-DOMt, and
the regular stacking platelet tactoids were maintained. A closer observation was given in Figure 9(c). The dark zones in this micrograph were the cross section of the silicate layers. The silicate layers were parallel to the surface of the films and dispersed uniformly in the RTV matrix. Individual thin layers of FR-DOMt were separated or intercalated by polymeric matrix. In addition, more organic species diffused into the holes of the dendrimer. [33] This was the evidence that this organoclay was mostly exfoliated in the RTV matrix.

**Conclusions**

RTV nanocomposites were prepared by solution intercalation between RTV and FR-DOMt additives.

The introduction of FR-DOMt improved the thermal stability and FR performance of RTV nanocomposites. RTV/FR-DOMt-3 showed better thermal stability than that of pure RTV. Its $T_{\text{onset}}$ was 310 °C, and was 100 °C higher than that of pure RTV. In addition, LOI values of these nanocomposites were increased from 22.0% to 28.0%. It showed the best fire protection when 15 phr of FR-DOMt were added. This FR property was better than that of RTV/Mt-15 nanocomposite.

RTV/FR-DOMt nanocomposites possessed better tensile properties. At loading of 3 phr of FR-DOMt, RTV nanocomposite showed the highest elongation at break, 500%. This was 46% higher than that of pure RTV. However, these tensile properties were not at all better than that of RTV/Mt-3 nanocomposite.

SEM and TEM images revealed that the majority of FR-DOMt particles dispersed homogeneously in RTV/FR-DOMt-3 and had a better affinity to the RTV matrix. This was ascribed to the stronger interactions between the organoclay and the macromolecules of silicone matrix.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was financially supported by ‘National Natural Science Funds [Project No.51173102]’.

**References**

[1] Jana RN, Nando GB, Khastgir D. Compatibilised blends of LDPE and PDMS rubber as effective cable insulators. Plast Rubber Compos: Macromol Eng. 2002;32:11–20.

[2] Mead JL, Tao Z, Liu HS. Insulation materials for wire and cable applications. Rubber Chem Technol. 2002;75:701–712.

[3] Fang SL, Hu Y, Song L, et al. Mechanical properties, fire performance and thermal stability of magnesium hydroxide sulphate hydrate whiskers flame retardant silicone rubber. J Mater Sci. 2008;43:1057–1062.

[4] Sepulcre-Guilabert J, Ferrandiz-Gomez TP, Martin-Martinez JM. Properties of polyurethane adhesives containing natural calcium carbonate+ fumed silica mixtures. J Adh Sci Tech. 2001;15:187–203.
[5] Jacobs JD, Koerner H, Heinz H, et al. Dynamics of alkyl ammonium intercalants within organically modified montmorillonite: dielectric relaxation and ionic conductivity. J Phys Chem. B. 2006;110:20143–20157.

[6] Xi YF, Zhou Q, Frost RL, et al. Thermal stability of octadecyltrimethylammonium bromide modified montmorillonite organoclay. J Colloid Interface Sci. 2007;311:347–353.

[7] Rabova V, Hron P. Effect of layered silicates on rheological and mechanical properties and thermal stability of high-molar mass polydimethylsiloxane matrix. E-Polymers. 2011;A91.

[8] Ding GF, Zhang CS, Shi YG, et al. Preparation and properties of silicone rubber/montmorillonite nanocomposites by melt intercalation process. China Elastomerics. 2006;16:47–50.

[9] Tan HM, Luo YJ. Dendritic polymers. Beijing: Chemical Industry Press; 2002.

[10] Dasgupta M, Peori MB, Kakkar AK. Designing dendritic polymers containing phosphorus donor ligands and their corresponding transition metal complexes. Coordin Chem Rev. 2002;233–234:223–235.

[11] Malik A, Chaudhary S, Garg G, et al. Dendrimers: a tool for drug delivery. Adv Biol Res. 2012;6:165–169.

[12] Wang JC, Sun K, Hao WL, et al. Structure and properties research on montmorillonite modified by flame-retardant dendrimer. Appl Clay Sci. 2014;90:109–121.

[13] Xia Y, Jian XG, Li JF, et al. Synergistic effect of montmorillonite and intumescent flame retardant on flame retardance enhancement of ABS. Polym-Plast Technol Eng. 2007;46:227–232.

[14] Yuan XH, Li XH, Zhu EB, et al. Synthesis and properties of silicone/montmorillonite nanocomposites by in-situ intercalative polymerization. Carbohydr Polym. 2010;79:373–379.

[15] Zhao Y, Wang JC. Preparation of novel hyperbranched flame-retardant polymer and its application into natural rubber systems. J Appl Polym Sci. 2013;128:3285–3294.

[16] Bi D, Li QF, Chen GX. Synthesis of polyhedral oligomeric silesquioxane-modified organic montmorillonites and their nanocomposites with poly(L-lactide). Appl Clay Sci. 2014;87:34–39.

[17] Zanetti M, Camino G, Reichert P. Thermal behaviour of poly(propylene) layered silicate nanocomposites. Macromol Rapid Comm. 2001;22:176–180.

[18] Camino G, Lomakin SM, Lageard M. Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms. Polymer. 2002;43:2011–2015.

[19] Jovanovic JD, Govedarica MN, Dvornic PR, et al. The thermogravimetric analysis of some polysiloxanes. Polym Degrad Stab. 1998;61:87–93.

[20] Thomas TH, Kendrick TC. Thermal analysis of polydimethylsiloxanes. I. Thermal degradation in controlled atmospheres. J Polym Sci: Part A-2: Polym Phys. 1969;7:537–549.

[21] Chen DZ, Yi SP, Wu WB, et al. Synthesis and characterization of novel room temperature vulcanized (RTV) silicone rubbers using Vinyl-POSS derivatives as cross linking agents. Polymer. 2010;51:3867–3878.

[22] Wang JC, Guo X, Wu D, et al. Research on the preparation of hyper-branched pentaerythritol (HPER) and its application in NR composites. China Elastomerics. 2012;22:59–62.

[23] Zanetti M, Camino G, Reichert P, et al. Thermal behaviour of poly(propylene) layered silicate nanocomposites. Macromol Rapid Comm. 2001;22:176–180.

[24] Zhang JH, Wang LF, Zhao YF. Improving performance of low-temperature hydrogenated acrylonitrile butadiene rubber nanocomposites by using nano-clays. Mater Design. 2013;50:322–331.

[25] Wang JC, Hao WL. Effect of organic modification on structure and properties of room-temperature vulcanized silicone rubber/montmorillonite nanocomposites. J Appl Polym Sci. 2013;129:1852–1860.

[26] Kaneko MLQA, Romero RB, Goncalves MDC, et al. High molar mass silicone rubber reinforced with montmorillonite clay masterbatches: morphology and mechanical properties. Eur Polym J. 2010;46:881–890.

[27] Shi XD, Gan ZH. Preparation and characterization of poly(propylene carbonate)/montmorillonite nanocomposites by solution intercalation. Eur Polym J. 2007;43:4852–4858.

[28] Qu L, Huang G, Wang Q, et al. Effect of diphenylsiloxane unit content on aggregation structure of poly(dimethylsiloxane-co-diphenylsiloxane). J Polym Sci Part B: Polym Phys. 2008;46:72–79.
[29] Ramli MR, Othman MBH, Arifin A, et al. Cross-link network of polydimethylsiloxane via addition and condensation (RTV) mechanisms. Part 1: synthesis and thermal properties. Polym Degrad Stab. 2011;96:2064–2070.

[30] Wang JC, Yang K, Xu N. Effect of intercalation agent on the structure and properties of OMMT and RTV/OMMT composites. J Appl Polym Sci. 2012;123:1293–1301.

[31] Chen DZ, Liu Y, Huang C. Synergistic effect between POSS and fumed silica on thermal stabilities and mechanical properties of room temperature vulcanized (RTV) silicone rubbers. Polym Degrad Stab. 2012;97:308–315.

[32] Vaia RA, Jandt KD, Kramer EJ, et al. Kinetics of polymer melt intercalation. Macromolecules. 1995;28:8080–8085.

[33] Halim KAA, Farrell JB, Kennedy JE. Preparation and characterisation of polyamide 11/montmorillonite (MMT) nanocomposites for use in angioplasty balloon applications. Mater Chem Phys. 2013;143:336–348.