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Graphical Abstract

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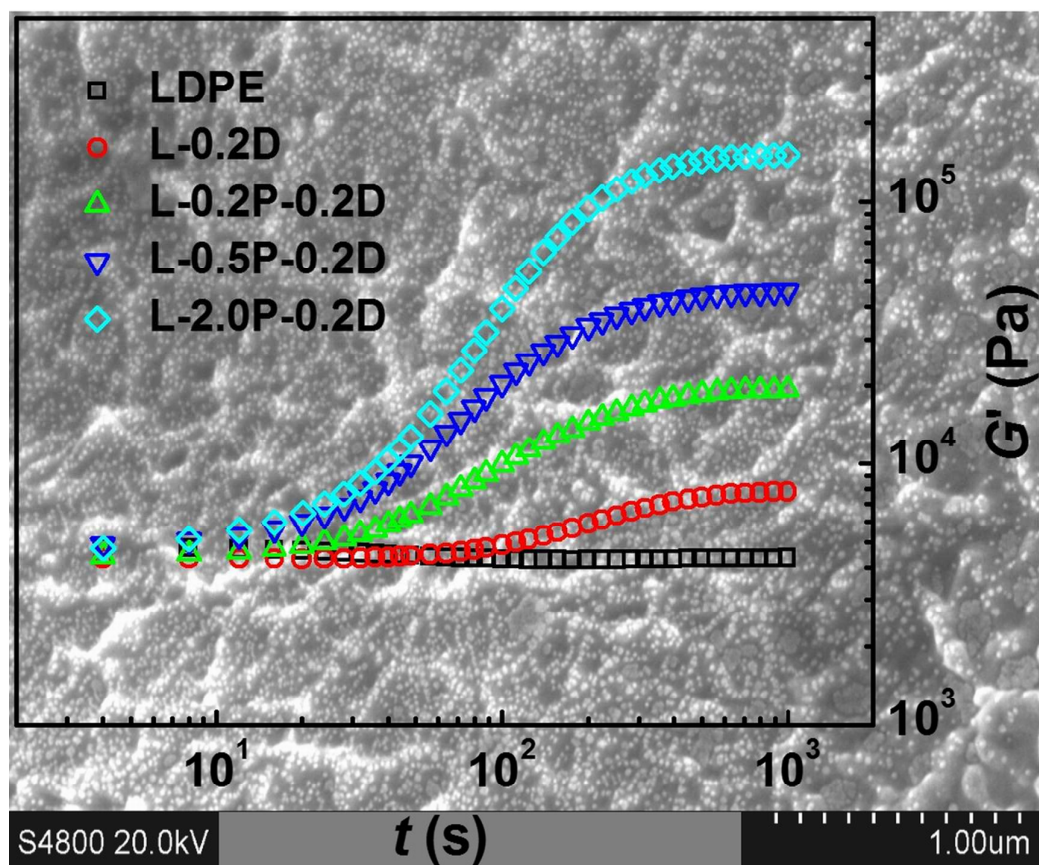
Jiachun Wu, Zi Liang Wu,* Hongmei Yang* and Qiang Zheng

ARTICLE TYPE

Crosslinking of low density polyethylene with octavinyl polyhedral oligomeric silsesquioxane as the crosslinker

Jiachun Wu, Zi Liang Wu,* Hongmei Yang* and Qiang Zheng

We report a new strategy for crosslinking of low density polyethylene (LDPE) by using a small amount of functional nanostructured hybrid agent, octavinyl polyhedral oligomeric silsesquioxane (OVPOSS), as the crosslinker, which dramatically decreases the amount of dicumyl peroxide (DCP) and thus avoids the
10 chain scission, scorch, and production of small pores in conventional peroxide crosslinking strategy. By melt blending under an extruder, OVPOSS aggregates with the size of tens of nanometers are homogeneously distributed in the matrix of LDPE, as confirmed by SEM. FTIR, DSC, and rheometer are used to study the crosslinking process and product properties. We found that vinyl groups of OVPOSS are firstly activated by the initiator of DCP and then react with LDPE to form an integrated network. The
15 crosslinking process is fast and highly efficient because each OVPOSS molecule has eight reactive vinyl groups. The reactions complete within 10 min at 175 $^{\circ}$C, which speed up as the increase in the content of DCP or OVPOSS. In the presence of 0.2 phr DCP, 0.5 wt% OVPOSS can effectively crosslink the composite sample with comparable properties to that with 2 phr DCP yet without OVPOSS. Thus obtained crosslinked LDPE should be suitable for high voltage cable materials. We believe that the
20 approach by using functional agents is powerful to crosslink or functionalize other polymers for special properties and applications.
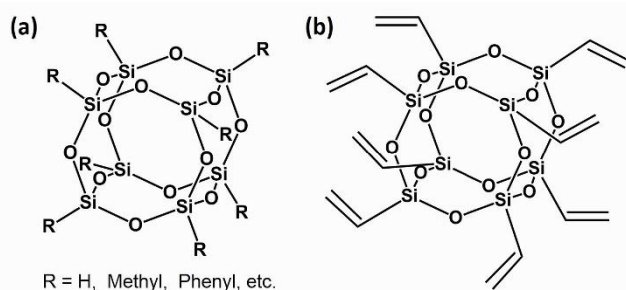
1. Introduction

Low density polyethylene (LDPE), as one of most common thermoplastic polymers, has been widely used as packing and
25 cable materials due to its excellent physical and electrical properties. However, LDPE has a major drawback in applications, the relatively low limitation of service temperature. To solve this problem, LDPE is usually crosslinked before use. Crosslinked LDPE possesses excellent dielectric properties, good resistance to
30 high-temperature deformation, and environmental stress cracking resistance,[1,2] which have made crosslinked LDPE useful for insulation medium to high voltage cables, hot water pipes, and heat shrinkable films.

There are mainly three approaches commercially used for
35 crosslinking LDPE: irradiation crosslinking (using high-energy radiation or electronics), peroxide crosslinking, and warm water crosslinking.[3,4] The peroxide crosslinking approach generally includes two steps: LDPE and peroxide are firstly physically blended at a relatively low temperature, and then crosslinked in a
40 special set-up with high temperature and pressure.[2] In contrast, warm silane crosslinking approach, in which silane molecules graft to the main chains of LDPE and crosslink LDPE by forming Si-O-Si bonds via hydrolysis and condensation reactions in warm water,[6,7] has a low cost of the set-up and materials, is easy to
45 process, and obtains products with good quality.[8,9] However, its

demerit is the side reactions such as chain extension occurred during the silane grafting,[10] which limits the applications of thus obtained products.

There are many efforts to study the methods of crosslinking
50 and properties of crosslinked LDPE, due to the significances in practical applications. To overcome the shortcomings mentioned above, researchers have made modifications to the strategies. For example, in peroxide crosslinking LDPE, the crosslinking mechanism,[11] effects on crosslinking process,[3,12] and rheological
55 behaviors of crosslinked LDPE[13] have been investigated. Furthermore, accessory crosslinker is added, to appropriately decrease the amount of peroxide, improve the crosslinking effect, and reduce the occurrence of side reactions.[14,15] On the other hand, in warm silane crosslinking approach, internal water-release
60 agent is used to avoid the inefficiency of water diffusion from the external environment. The effects of silane molecular structures and grafting degree on the crosslinking process have been systematically studied.[16] Beside silane molecules, many other agents, including difunctional or trifunctional electron-rich
65 olefins such as tetramethyltetravinylcyclotetrasiloxane, triallyl isocyanurate, and triallyl cyanurate, can be used as accessory crosslinkers.[14] In the existence of radicals, these accessory agents have high reactivity and are easy to graft to polymer chains,[15] which improve the crosslinking efficiency and affect the structure
70 of crosslinked polymer. Several groups have reported that the

Scheme 1 Molecular structures of POSS (a) and OVPOSS (b).

multifunctional molecules form "coagent bridges" during the crosslinking reaction.[17-19] Although there are many efforts on crosslinking LDPE by introducing accessory agents, using functional organic-inorganic hybrid agent as the crosslinker is rarely reported.

Polyhedral oligomeric silsesquioxane (POSS) with molecular formula of $(RSiO_{1.5})_m$, in which m is equal to 6, 8, 10, or 12 (Scheme 1a), is one hybrid molecule containing nanostructured Si-O skeleton and surface-anchored organic groups, R, which can be inert such as methyl and phenyl groups or functional such as vinyl and epoxy groups.[20,21] Therefore, POSS is easily to be composite with polymers by blending, grafting, and copolymerization,[22,23] to improve the material properties such as the heat resistance, oxidation resistance, mechanical properties, and dielectrical properties.

When R on the angle Si atoms is inert, POSS cannot be incorporated into polymeric matrix by chemical bonding. However, myriad composite materials are developed by physical blending and possess special properties.[24-27] Huang et al. have reported the improvement in dielectrical properties of composite materials of octavinyl polyhedral oligomeric silsesquioxane (OVPOSS, Scheme 1b) and LDPE by physical blending.[28] When R is active, POSS with multiple functional groups can joint several polymer chains by grafting reaction to form a chemically crosslinked network, which has been used in preparing elastomers[29,30] and hydrogels.[31-33] Zhang and his colleagues have studied the preparation and properties of POSS filled polypropylene by physical blending and grafted polypropylene by reactive blending, as well as their differences.[34-37] However, to our best knowledge there are no studies on the crosslinking process and mechanism of polyolefin by using a small content of OVPOSS as the crossliner.

In this paper, we report a new strategy to prepare crosslinked LDPE by using OVPOSS, a functional organic-inorganic hybrid agent, as the crosslinker. In this process, only a small amount of peroxide is needed to initiate the crosslinking reaction, so that the demerit in peroxide crosslinking approach can be properly relieved. Scanning electronic microscopy (SEM) is applied to observe the size and distribution of OVPOSS aggregates in LDPE before and after the crosslinking. Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and rheometer are used to monitor the crosslinking process and effectiveness. A rational crosslinking mechanism is formulated based on the experimental results. This work presenting a novel approach to prepare crosslinked LDPE should merit preparing other polyolefins with improved properties and broader applications.

2. Experimental

2.1 Materials

LDPE used in this work (with a density of 0.92 g/cm³, $M_n = 1.4 \times 10^4$, $M_w = 7.3 \times 10^4$, and a melting flow index of 4.2 g/10 min at 2.16 kg and 190 °C) was purchased from Sinopec Yanshan Petrochemical Company (Beijing, China) and soaked in ethanol at 50 °C for 5 h before use. Dicumyl peroxide (DCP, Virtulla Tech. Co. Ltd., China) and vinyltrimethoxysilane (Nanjing Xiangqian Chemical Co. Ltd., China) were used as received. The ultrapure water was made in the lab. All other solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and used without further purification.

2.2 Sample Preparation

2.2.1 Synthesis of octavinyl polyhedral oligomeric silsesquioxane (OVPOSS)

OVPOSS was synthesized according to a modified classic route (Fig. S1 in Supporting Information).[38,39] To a 500 mL three-necked bottle was added anhydrous methanol (200 mL), Milli-Q water (18.2MΩ cm, 9 mL), and concentrated hydrochloric acid (36 wt%, 2 mL, as the catalyst). The formed mixture (mixture 1) was stirred rapidly at 40 °C. To a 100 mL beaker was added vinyltrimethoxysilane (20 mL) and anhydrous methanol (50 mL). The formed homogeneous mixture (mixture 2) was transferred into a 100 mL constant pressure funnel. Then mixture 2 was added dropwise to mixture 1 within 4 h, followed by addition of 30 mL anhydrous methanol. The resulting mixture was stirred for another 5 d at 40 °C. The precipitate was filtered and purified further by dissolving in tetrahydrofuran and then depositing in ethanol. Thus obtained OVPOSS was a white crystal powder with high quality, as characterized by nuclear magnetic resonance (NMR) (Fig. S2), FTIR (Fig. S3), and X-ray diffraction (XRD) (Fig. S4).

Table 1 Composition and sample code of LDPE/OVPOSS/DCP composites.

LDPE content (wt%)	OVPOSS content (wt%)	DCP content (phr)	Sample code
100	0	0	LDPE
100	0	0.1	L-0.1D
100	0	0.2	L-0.2D
100	0	0.5	L-0.5D
100	0	0.8	L-0.8D
100	0	1.0	L-1.0D
100	0	2.0	L-2.0D
99.8	0.2	0	L-0.2P
99.8	0.2	0.1	L-0.2P-0.1D
99.8	0.2	0.2	L-0.2P-0.2D
99.8	0.2	0.5	L-0.2P-0.5D
99.5	0.5	0	L-0.5P
99.5	0.5	0.2	L-0.5P-0.2D
99.5	0.5	0.5	L-0.5P-0.5D
98	2.0	0	L-2.0P
98	2.0	0.2	L-2.0P-0.2D
98	2.0	0.5	L-2.0P-0.5D

2.2.2 Preparation of the composite samples

LDPE (100 phr) and DCP (5 phr) were put into a flask of 250 ml and mixed through a rotary evaporator at 80 °C. DCP was coated homogenously on the surface of LDPE granules to produce a
5 DCP carrier. The DCP carrier was then blended using a co-rotating twin-screw extruder (PRISM TSE 16 TC, Thermo Scientific, Waltham, UK) to obtain masterbatches of DCP. The masterbatches of OVPOSS (10 g) in LDPE (90 g) were prepared on the twin-screw extruder by melt blending. The extrusion
10 conditions are shown in Table S1.

The crosslinkable composite samples were prepared by melt extrusion of LDPE and masterbatches of DCP and OVPOSS in suitable ratios to get the prescribed compositions in Table 1 in the twin-screw extruder. Samples are coded as L-xP-yD, in which x
15 and y are the content of OVPOSS in wt% and DCP content in phr, respectively. Samples without DCP and OVPOSS are coded as L-xP and L-yD, respectively.

2.3 Characterization

20 2.3.1 SEM-EDS

Scanning electron microscopy (SEM; Hitachi-S4800) with energy dispersive spectroscopy (EDS) was used to characterize the dispersion state of OVPOSS in the composite materials before and after crosslinking. Crosslinkable and crosslinked samples,
25 prepared on a compression-molding machine under 15 MPa for 10 min at 115 and 175 °C, respectively, were broken in liquid nitrogen and then dried in a vacuum oven. The fracture surfaces of the samples were coated with gold by vapor deposition using a Denton Desk-1 vacuum sputter coater for SEM observation and
30 X-ray element mapping of silicon.

2.3.2 FTIR

Infrared spectra of the thin film samples were obtained at ambient temperature with a Fourier transform infrared spectroscopy
35 (Vector 22 FT-IR spectrum, Bruker, Germany). Single beam spectra of the samples were obtained after an average of 31 scans between 4000 and 400 cm^{-1}. All spectra were obtained in the transmittance mode.

40 2.3.3 DSC

The crosslinking process, crystallization and melting behaviors of the samples were analyzed using a Q100 (TA instruments) differential scanning calorimeter (DSC) in a flowing nitrogen atmosphere. All the samples, weighted around 5 to 10 mg, were
45 sealed in standard aluminum capsules and heated from 40 to 220 °C. Then the samples were cooled from 220 to 40 °C and reheated from 40 to 180 °C. All the heating and cooling rates were kept at 10 °C/min. The crystallinity of the samples, X_c, was determined by the following equation

$$50 \qquad X_c = \frac{\Delta H_f}{\Delta H_m (1-\Phi)} \qquad (1)$$

and the thickness of the lamellar crystal of LDPE, Δl_c, can be determined by the empirical Gibbs-Thompson equation[40]

$$T_m = T_m^0 (1 - \frac{2\sigma}{\Delta H_m \cdot \Delta l_c}) \qquad (2)$$

in which, ΔH_f is the enthalpy changes obtained from the heat of

55 fusion in melting; ΔH_m is the enthalpy changes in melting of a 100% crystalline sample; Φ is the weight fraction of OVPOSS and DCP in the samples; T_m is the melting point of the samples; T_m^0 is the equilibrium melting point of polymer; σ is the chain folding energy of polyethylene. For LDPE used in this work,
60 ΔH_m, T_m^0, and σ are 293 J/g, 417.15 K, and 93.4 erg/cm^2, respectively.[41]

2.3.4 Rheological measurements

An advanced rheometric expansion system (ARES-G2, TA,
65 USA), operated with 25 mm parallel plate setup, was used to measure the angular frequency dependence of storage modulus (G'), loss modulus (G''), loss tangent (tanδ), and complex viscosity (η^*) of the compounds in the range of 100-0.015 rad/s. Strain sweep in the range of 0.01-100% was performed to
70 determine the linearity region of crosslinked LDPE. The frequency sweep was tested at a strain of 1% to measure the linear viscoelasticity of crosslinked LDPE. For rheological tests, circular disk-like samples of 25 mm in diameter and 1.2 mm in thickness were prepared on a compression-molding machine
75 under 15 MPa for 10 min at 175 °C, then transferred into another compression-molding machine under 15 MPa for 5 min at ambient temperature. All the rheological tests mentioned above were operated at 150 °C, above T_m of the samples.

Time sweep was used to test the crosslinking behavior, in
80 which the samples were prepared previously at 115 °C in the compression-molding machine. The samples were stored at room temperature for at least 48 h before the testing at 175 °C.

3. Results and Discussion

3.1 OVPOSS crosslinking reaction and its mechanism

85 To obtain crosslinked LDPE, peroxide-curing reaction based on radical coupling mechanism is the most common method. However, using DCP to crosslink polyolefin is always accompanied with side reactions such as chain scission and scorch at high temperature and production of small pores.[42,43]
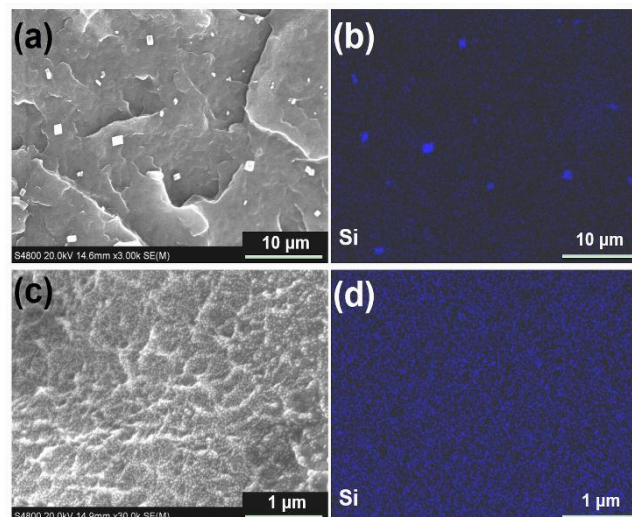90 These issues can be properly addressed by using OVPOSS as the

Figure 1 SEM images (a,c) and corresponding elemental mapping images (b, d) of the fracture surface of L-0.2P-0.2D before (a,b) and after (c,d) crosslinking.

crosslinker, in which only a small amount of DCP is needed as the initiator.

The morphology of the fracture surface of crosslinkable and crosslinked samples (L-0.2P-0.2D) is shown in Fig. 1 and Fig. S5. Before crosslinking, OVPOSS crystals with cuboid shape and size ranging from hundreds of nanometers to several micrometers are randomly dispersed in the matrix (Fig. 1a and Fig. S5a). However, after crosslinking, OVPOSS aggregates break to small particles with the size of tens of nanometers (Fig. 1c, Figs. S5b and S5c).[35] Elemental mapping images (Figs. 1b and 1d) indicate that the particles are just OVPOSS aggregates. We found that the breaking of micron-sized OVPOSS crystals to nano-sized particles is not due to high temperature but closely related to the crosslinking reaction, because without DCP to trigger the reaction, the morphology and size of OVPOSS aggregates in L-0.2P have no changes after the same heating process (Figs. S5d-5f). We also found micron-sized OVPOSS particles in the mixture of OVPOSS and DCP disaggregated into nano-sized particles after the thermal initiated reaction (Fig. S6); in the reaction process, there is a small exothermic peak at ~145 $^{\circ}$C besides the main peak at ~170 $^{\circ}$C (Fig. S7). DCP starts to decompose at ~145 $^{\circ}$C, which triggers the reaction of vinyl groups at the surface of OVPOSS aggregates. The reaction would produce localized heat and change the crystalline morphology. If these differences between the outer and inner crystals of OVPOSS are big enough, the aggregates will break into small pieces. In consequence, a large amount of OVPOSS molecules are exposed and have the chance to connect with radicals. The following reaction generates more heat and forms the second large exothermic peak at 170 $^{\circ}$C. In the presence of DCP, the well dispersed OVPOSS molecules and nano-sized particles with multiple vinyl groups will act as an
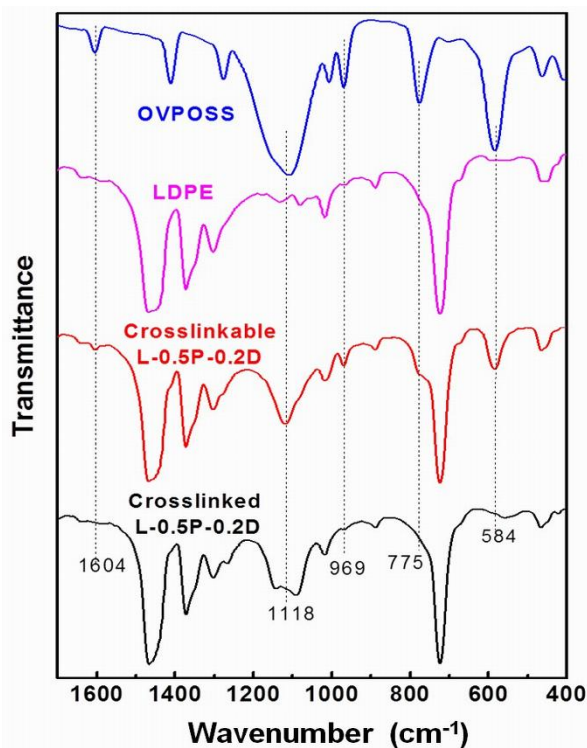

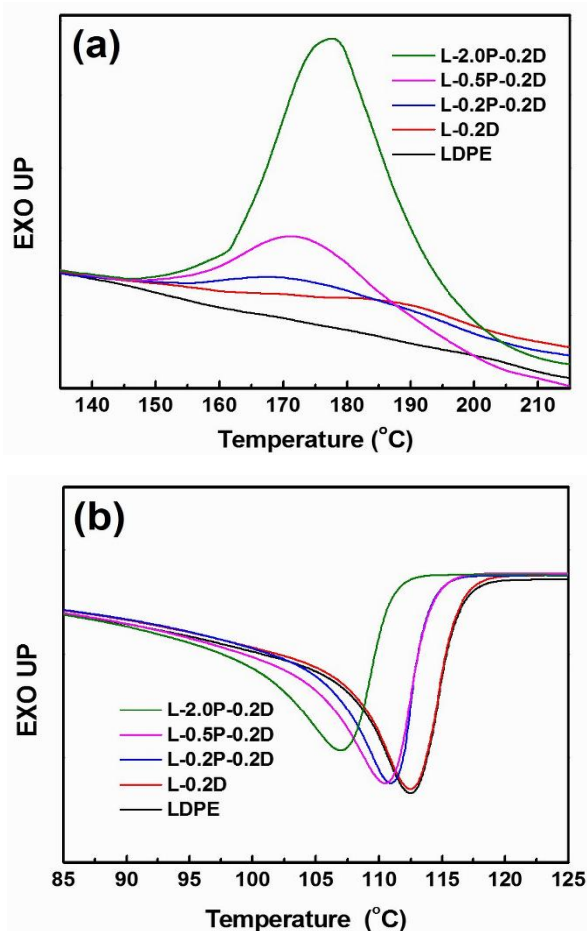**Figure 2** FTIR spectra of the OVPOSS, LDPE, crosslinkable and crosslinked L-0.5P-0.2D.

Figure 3 DSC thermograms of crosslinkable LDPE during the heating process. (a) L-xP-0.2D, during the crosslinking; (b) L-xP-0.2D, after the crosslinking. Heating rate: 10 $^{\circ}$C/min.

effective crosslinker to crosslink LDPE.

Fig. 2 shows FTIR spectra of the pure LDPE, OVPOSS, and the composite sample (L-0.5P-0.2D) before and after the crosslinking process. In contrast with the pure LDPE, several characteristic peaks of OVPOSS exist in the spectrum of crosslinkable L-0.5P-0.2D (before crosslinking). The peaks at 1604, 1118, and 775 cm^{-1} correspond to the absorption of $v_{C=C}$, $v_{Si-O-Si}$, and $v_{Si-C=C}$, respectively. The peaks at 969 and 584 cm^{-1} correspond to the absorption of the stretching vibration of trans-vinylene and to the fingerprint spectrum of Si-O-Si skeleton vibration, respectively. By comparision of the two spectra, we can see that characteristic peaks of OVPOSS appear in the right places of the spectrum of composite material prepared by melt blending. After the crosslinking, there are several notable changes of the peaks due to the reaction-induced variations of chemical environment of some groups: (i) the peaks at 1604 and 969 cm^{-1} almost disappear, indicating that most of vinyl groups have been reacted; (ii) the peak at 1118 cm^{-1} has evident change from a single peak to two split peaks, mainly due to the destruction of perfect symmetry of Si-O skeleton; (iii) the disappearance of peak at 584 cm^{-1} is also due to the reaction-induced variation of chemical environment for Si-O-Si bond; (iv) the peak at 775 cm^{-1}, which is partially hidden by the broad peak of LDPE at 730 cm^{-1}, has a detectable change, due to the transformation from Si-C=C to Si-C-C. Based on these results, we conclude that most vinyl

groups of OVPOSS have reacted and been incorporated into the polymeric matrix of crosslinked LDPE. It is expected that OVPOSS effectively links LDPE chains to form a network.

The crosslinking process is also investigated in situ by using DSC. The crosslinkable samples (L-xP-0.2D and L-0.2P-yD) are sealed in the aluminum capsules; crosslinking reaction takes place during the first heating process up to 220 $^\circ$C. As shown in Fig. 3a, the exothermic peak of composite sample with 0.2 wt% OVPOSS (L-0.2P-0.2D) moves to low temperature, when compared to that of L-0.2D sample without OVPOSS. As the content of OVPOSS increases, the exotherm rapidly increases, indicating the effective crosslinking reaction of OVPOSS.

We should note that the peroxide crosslinking process of LDPE without OVPOSS shows an exothermic peak at an identical temperature, ca. 190 $^\circ$C. However, the exothermic peaks in our systems with OVPOSS appear at relatively low temperature. Furthermore, the peak slightly moves to high temperature when the content of OVPOSS increases from 0.2 to 2 wt% (Fig. 3a). These differences suggest a different crosslinking mechanism in our work.

Essentially, the peroxide crosslinking of LDPE is a multiple-step reaction. The DCP decomposes into free radicals at an appropriate temperature, which capture hydrogen atoms from the polyethylene chains. The polymer chains then become macroradicals, which couple to form a crosslinked polymeric network.[11,44] However, in our work, the radicals from decomposition of DCP preferentially react with the active vinyl groups of OVPOSS, which should have a lower energy than taking a hydrogen from the main chain of LDPE (Fig. 4). This is supported by the DSC results (Fig. 3a and Fig. S7), i.e. the exothermic peaks of crosslinking LDPE with OVPOSS move to low temperature. The exothermic peak of L-0.2P-0.2D is ~170 $^\circ$C, 20 $^\circ$C lower than that of L-0.2D. The radical of OVPOSS can take a hydrogen from LDPE chain, leading to the formation of polyethylene network. We should note that part of DCP radicals also can capture a hydrogen from LDPE main chain to form macroradicals, which couple each other or with OVPOSS radicals to form a network (Fig. 4). By introducing OVPOSS as the main crosslinker, we can dramatically decrease the amount of DCP and therefore avoid the possibility of chain scission and the amount of side product from DCP decomposition.

The crosslinking of LDPE by OVPOSS results in rational modification of the product properties. DSC is also applied to investigate the melting temperature, T_m, and crystallinity, X_c, of
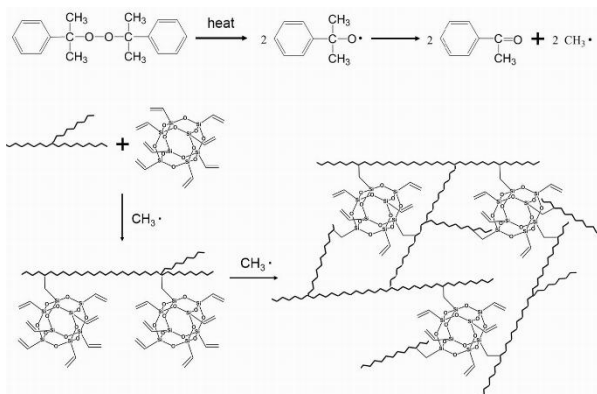
Table 2 Melting and crystalline parameters of crosslinked LDPE samples with 0.2 phr DCP, L-xP-0.2D.

Samples	T_c ($^\circ$C)	T_m ($^\circ$C)	Δl_c (nm)	ΔH_f (J/g)	X_c (%)
LDPE	98.8	112.0	8.90	114.5	39.1
L-0.2D	98.3	111.8	8.83	109.3	37.4
L-0.2P-0.2D	97.6	111.0	8.61	107.1	36.7
L-0.5P-0.2D	96.8	110.5	8.50	105.4	36.2
L-2.0P-0.2D	93.6	107.0	7.70	97.0	33.9

Table 3 Melting and crystalline parameters of crosslinked LDPE samples with 0.2 wt% OVPOSS, L-0.2P-yD.

Samples	T_c ($^\circ$C)	T_m ($^\circ$C)	Δl_c (nm)	ΔH_f (J/g)	X_c (%)
LDPE	98.8	112.0	8.90	114.5	39.1
L-0.2P	98.4	111.8	8.83	114.5	39.1
L-0.2P-0.1D	97.9	111.2	8.68	109.8	37.6
L-0.2P-0.2D	97.6	110.9	8.61	107.1	36.7
L-0.2P-0.5D	96.9	110.1	8.40	104.7	36.0

crosslinked LDPE (Fig. 3b). Two serials of samples, L-xP-0.2D and L-0.2P-yD, are used to study the effect of OVPOSS and DCP on T_m and X_c. The typical melting and crystalline parameters including T_m, crystallization temperature T_c, the thickness of the lamellar crystal Δl_c, and X_c obtained from the melting endotherms are given in Table 2 and Table 3. The crosslinking leads to slight decrease in T_m, Δl_c, and X_c, less than 2 $^\circ$C, 0.4 nm, and 3%, respectively, due to the restricted chain mobility and folding to form crystal domain. Only when the sample contains a relatively large content of OVPOSS (2 wt% in L-2.0P-0.2D), the melting peak shows notable change, corresponding to 5 $^\circ$C T_m, 1.13 nm Δl_c, and 5% X_c lower than those of L-0.2D.

3.2 Dynamic rheology of samples during and after crosslinking

The crosslinking process of LDPE with OVPOSS, leading to the formation of an integrated network and variation of mechanical properties, is investigated by dynamic rheology.
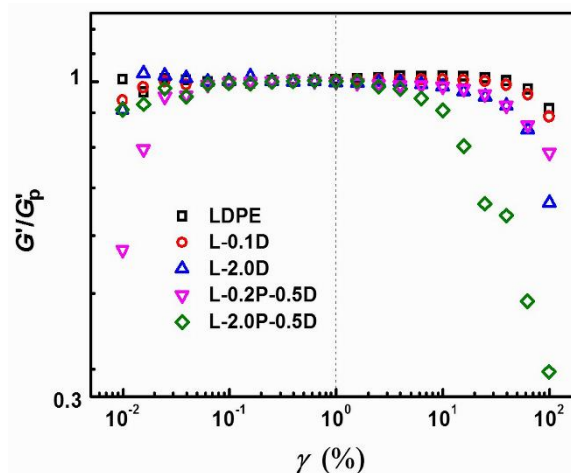

Figure 5 Normalized storage modulus, G'/G'_p, as a function of strain amplitude, γ, for pure LDPE and crosslinked LDPE with different content of OVPOSS and DCP at 150 $^\circ$C. Frequency, ω, is 3.14 rad/s.

Figure 4 Reaction scheme of OVPOSS crosslinked LDPE.

3.2.1 Strain sweep of crosslinked LDPE

Strain sweep with strain amplitude, γ, ranging from 0.01% to 100% is performed on the samples of pure LDPE and crosslinked samples at 150 $^{\circ}$C, above their T_{m}. Fig. 5 shows the normalized

[5] storage modulus (G'/G'_{p}) as a function of γ. Here, G' and G'_{p} are the storage modulus and the value in the linearity region. At frequency, ω, of 3.14 rad/s, G'/G'_{p} was found to be stable at $\gamma < 33\%$ for pure LDPE, whereas the critical γ for onset of nonlinearity decreases to 16%, 16%, and 6% for L-2.0D, L-0.2P-

[10] 0.5D, and L-2.0P-0.5D, respectively. All the following dynamic tests are performed at $\gamma = 1\%$.

3.2.2 Rheologic behaviors during the crosslinking process

Fig. 6a shows G' as a function of the crosslinking time, t, at 175

[15] $^{\circ}$C for crosslinkable samples of L-xP-0.2D. G' increases with t and achieves a constant value after 10 min, indicating the completion of crosslinking reaction. With a constant content of DCP, 0.2 phr, the equilibrium modulus, G'_{e}, increases with the content of OVPOSS. With incorporation of 0.5 wt% OVPOSS,

[20] G'_{e} of L-0.5P-0.2D is 6 times that of L-0.2D (Table 4).

Fig. 6b shows G' as a function of t at 175 $^{\circ}$C for crosslinkable samples of L-0.2P-yD. G' also increases with t and achieves a
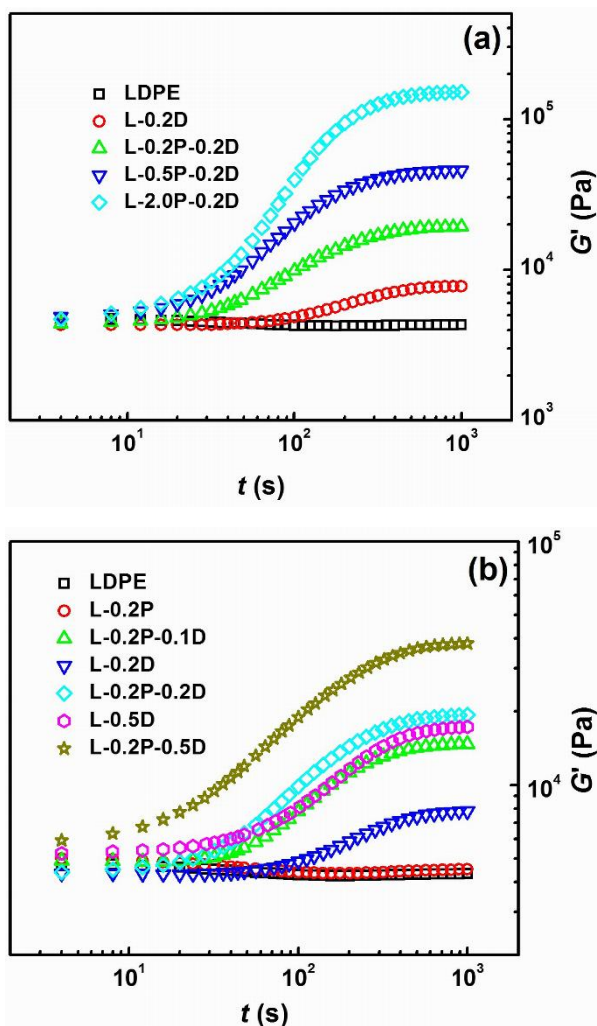

[25] **Figure 6** G' as a function of crosslinking time, t, at a temperature of 175 $^{\circ}$C for samples of LDPE, L-xP-0.2D (a), and L-0.2P-yD (b). Corresponding G' of L-yD is also shown for a comparision.

Table 4 Equilibrium modulus, G'_{e}, and gelation time, t_{g}, of L-yD and L-xP-yD.

Samples	G'_{e} (kPa)	t_{g} (s)
LDPE	4.4	--
L-0.2P	4.5	--
L-0.2D	7.8	--
L-0.5D	17.3	138
L-0.2P-0.1D	14.7	128
L-0.2P-0.2D	19.4	80
L-0.5P-0.2D	45.7	44
L-2.0P-0.2D	151.5	35
L-0.2P-0.5D	38.1	24

constant value after 10 min. With a constant content of OVPOSS,
[30] 0.2 wt%, G' increases with the content of DCP. Even a small amount of OVPOSS can dramatically increase G'_{e}. The incorporation of 0.2 wt% OVPOSS (L-0.2P-0.2D) leads to G'_{e} 3 times that without OVPOSS (L-0.2D). G'_{e} of L-0.2P-0.1D is around 2 times that of L-0.2D; G'_{e} of L-0.2P is almost the same as
[35] that of pure LDPE (Table 4). These results indicate that OVPOSS effectively crosslinks the polyethylene chain, which can only been triggered in the presence of DCP (Fig. 6b). G'_{e} of L-0.5D is between the values of L-0.2P-0.1D and L-0.2P-0.2D (Table 4). For a better crosslinking of LDPE, an optimal combination
[40] between the contents of OVPOSS and DCP is needed.

During the crosslinking, G' and the loss modulus, G'', increase with t in different speeds and cross each other after a certain time. The gelation time at $G' = G''$, t_{g}, is extracted as a special parameter to characterize the crosslinking speed, which is also
[45] listed in Table 4. t_{g} for L-0.5D is 138 s, however, with incorporation of 0.2 wt% OVPOSS, t_{g} for L-0.2P-0.5D is shortened to 24 s, indicating high crosslinking efficiency of OVPOSS. For L-xP-0.2D, t_{g} decreases from 80 s to 35 s with the increase in OVPOSS content from 0.2 to 2.0 wt%. For L-0.2P-yD,
[50] t_{g} shortens from 128 s to 24 s with the increase in DCP content from 0.1 to 0.5 phr. It is interesting to note that t_{g} for L-2.0P-0.2D is longer than that for L-0.2P-0.5D, while the G'_{e} is almost 4 times that of the latter. These results suggest that the crosslinking speed and t_{g} are mainly determined by the amount of DCP (the initiator),
[55] whereas the corsslinking degree and G'_{e} are mainly determined by the content of OVPOSS (the crosslinker).

3.2.3 Rheologic behaviors of crosslinked LDPE

The reactions in the presence of DCP and OVPOSS with different
[60] content produce branched chains or crosslinked network of LDPE with different extent. According to Winter's theory,[45-47] at gel point with the first appearance of an integrated network, the rheological behavior of a polymer could be characterized by "self-similar relaxation pattern". For critical gel, its viscoelastic
[65] parameters are shown to be related as

$$G'(\omega) = \frac{G''(\omega)}{\tan(n\pi/2)} = S\Gamma(1-n)\cos(n\pi/2)\omega^n \qquad (3)$$

where S is gel strength, n is the relaxation exponent whose value

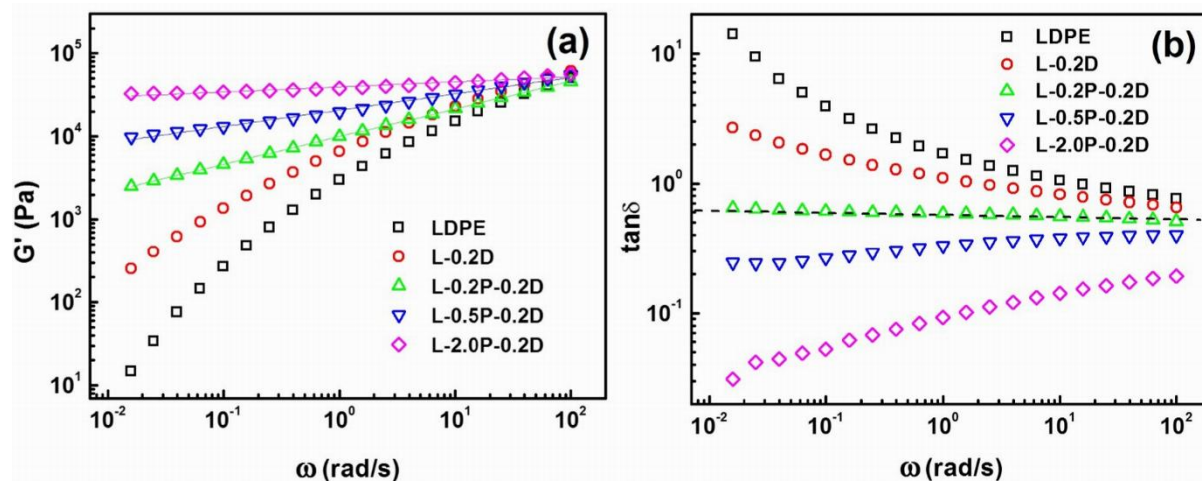**ARTICLE TYPE**

Figure 7 G' (a) and $\tan\delta$ (b) as a function of ω for crosslinked samples of L-xP-0.2D at 150 °C. The solid lines in (a) are drown according to eq. (3).
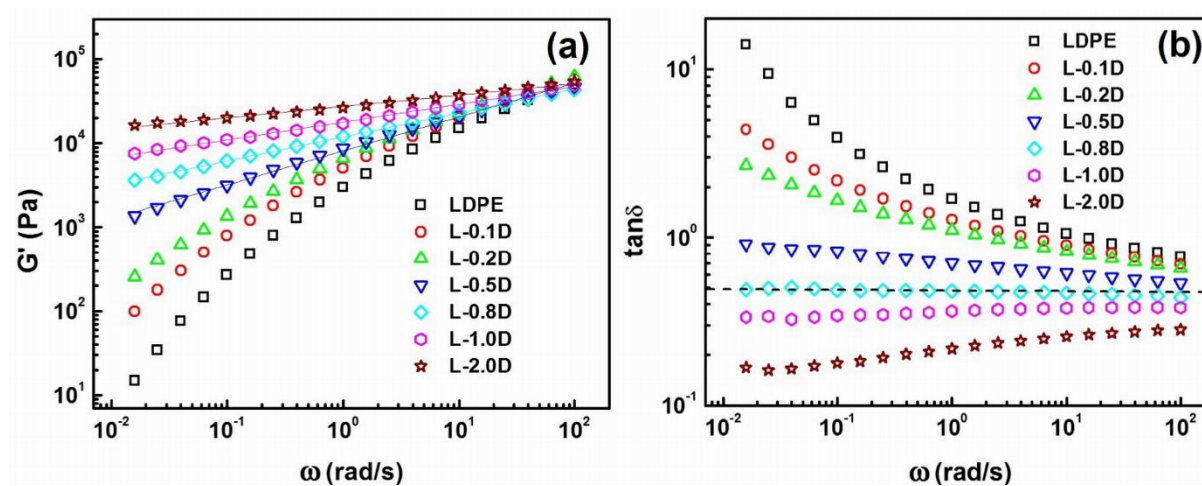

5 **Figure 8** G' (a) and $\tan\delta$ (b) as a function of ω for crosslinked samples of L-yD at 150 °C. The solid lines in (a) are drown according to Eq. (3).

lies between 0 and 1, $\Gamma(1\text{-}n)$ is the gamma function.

At the critical gel point, when $0 < \omega < 1/\lambda_0$, $\tan\delta$ becomes frequency independent, i.e.

$$\tan\delta = \frac{G''}{G'} = \tan\left(\frac{n\pi}{2}\right) \qquad (4)$$

10 λ_0 is the relaxation time of the transition from rubbery plateau to the reputation regime in the low-frequency zone. This typical characteristic of the critical gel provides us with an easy tool to determine the gel point using rheological methods, i.e., in a $\tan\delta$ versus ω plot, the gel point manifests itself by the appearance of a 15 plateau with zero slope. Typically, for polymer melts the slopes of curves in a $\tan\delta$ versus ω plot are negative while for the solids (gels) it is positive. Hence, the transition from melt to gel can be easily identified if a change from negative to positive slope appears in a $\tan\delta$ versus ω plot.

20 Fig. 7 shows G' and $\tan\delta$ as a function of ω for crosslinked samples of L-xP-0.2D at 150 °C. Pure LDPE exhibits a non-terminal flow characterized by $G' \sim \omega^{1.50}$ and $G'' \sim \omega^{0.86}$ at frequency $\omega < 0.2$ rad/s due to the wide molecular weight distribution of LDPE ($M_w/M_n = 5.14$). The crosslinking not only 25 elevates G' and depresses $\tan\delta$ over the whole ω range, but also leads to the fluid-to-solid transition, as shown by the gradually diminished ω-dependence of G' with the increase in OVPOSS content (Fig. 7a). The $\tan\delta$ curves of crosslinked LDPE exhibit negative slopes when the content of OVPOSS is less than 0.2 30 wt%, and positive slopes when the content OVPOSS is more than 0.2 wt% (Fig. 7b). For L-0.2P-0.2D, $\tan\delta$ with a constant value of 0.6 is independent of ω. Therefore, 0.2 wt% of OVPOSS is the critical value for the samples of L-xP-0.2D to form an integrated n e t w o r k .
35 In comparison, the curves of G' and $\tan\delta$ versus ω for samples

of L-*x*P show that OVPOSS physically modified LDPE can only slightly elevate *G′* (Fig. S8a). The slopes of the tan*δ* versus *ω* curves keep negative for the physical blending samples (Fig. S8b), indicating no network existed in these samples. Fig. 8 shows *G′* and tan*δ* as a function of *ω* for crosslinked samples of L-*y*D. *G′* of the samples increases with DCP content at low *ω*, yet its *ω*-dependence gradually decreases as *ω* increases (Fig. 8a). Without OVPOSS, 0.8 phr of DCP is the critical value to form an integrated network (Fig. 8b); its tan*δ* keeps an constant value of 0.5. The sample with 2 phr DCP (L-2.0D) exhibits the same rheological behaviors to those of L-0.5P-0.2D, indicating a similar crosslinking effect. These results prove further the high efficiency of OVPOSS as the crosslinker in crosslinking LDPE.

Different from other composite materials by using POSS as the fillers to improve the mechanical or electrical properties, in our work OVPOSS is used as a crosslinker and incorporated to the polymer matrix. Therefore, the amount of OVPOSS as crosslinker (0.2-2 wt%) is much less than other POSS as fillers (usually > 15 wt%). The corresponding properties of POSS such as oxidation resistance and flame resistance are not pronounced in our systems. However, as we presented above, OVPOSS as a special crosslinker is of high efficiency in crosslinking LDPE. This strategy can be generalized to other systems, by using different functional agents such as carbon nanotube and graphene to modify polymers, elastomers, hydrogels, etc.[48-50]

4. Conclusions

In this paper, we present the crosslinking of LDPE with a small amount of functional nanostructured hybrid molecule, OVPOSS, as the crosslinker, which effectively decreases the content of DCP and avoids the side reaction and production of small pores in the peroxide crosslinking approach. SEM and elemental mapping results show that OVPOSS aggregates, with the content of 0.2-2 wt% and the size ranging from tens of nanometers to several micrometers, are dispersed homogeneously in LDPE matrix after melt blending and croslinking. The crosslinking process between OVPOSS and LDPE has been monitored by FTIR, DSC, and rheometer. We have rationally contented a crosslinking mechanism: the radicals from DCP decomposition preferentially react with the vinyl groups of OVPOSS and then graft to LDPE chains to from a three dimensional network. The crosslinking speed increases with DCP content, whereas crosslinking degree increases with OVPOSS content. Therefore, an optimal combination of OVPOSS and DCP is needed for better corsslinking. The crosslinking leads to increase in storage modulus, *G′*, and decrease in the thickness of the lamellar crystal of polyethylene due to the restricted chain mobility and folding to form crystal domain. The sample with 0.5 wt% OVPOSS and 0.2 phr DCP (L-0.5P-0.2D) exhibits the same rheological behaviors as that with 2 phr DCP prepared by the conventional peroxide crosslinking (L-2.0D). This work describes a new strategy to crosslink LDPE by using functional hybrid agents as the corsslinker, which should be suitable for crosslinking or functionalization of other polymers towards specific applications.

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Notes and references

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1   S. Dadbin, M. Frounchi, M. H. Saeid and F. Gangi, *Journal of Applied Polymer Science*, 2002, **86**, 1959.
2   A. Smedberg, T. Hjertberg and B. Gustafsson, *Polymer*, 1997, **38**, 4127.
3   L. H. U. Andersson and T. Hjertberg, *Polymer*, 2006, **47**, 200.
4   A. Smedberg, T. Hjertberg and B. Gustafsson, *Polymer*, 2003, **44**, 3395.
5   Y. T. Shieh and T. H. Tsai, *Journal of Applied Polymer Science*, 1998, **69**, 255.
6   H. C. Kuan, J. F. Kuan, C. C. M. Ma and J. M. Huang, *Journal of Applied Polymer Science*, 2005, **96**, 2383.
7   P. Pollet, C. L. Liotta, C. A. Eckert, M. Verma, E. Nixon, S. Sivaswamy, R. Jha, F. Momin, L. Gelbaum, B. I. Chaudhary and J. M. Cogen, *Industrial & Engineering Chemistry Research*, 2011, **50**, 12246.
8   S. Dalai and W. X. Chen, *Journal of Applied Polymer Science*, 2002, **86**, 1296.
9   Z. H. Li, G. H. Hu, J. P. Corriou, S. Hoppe, C. Fonteix, R. Laine, J. Habimana and D. Deheunynck, *Polymer Engineering and Science*, 2013, **53**, 1571.
10 C. M. Jiao, Z. Z. Wang, X. M. Liang and Y. Hu, *Polymer Testing*, 2005, **24**, 71.
11 B. Likozar and M. Krajnc, *Polymer Engineering and Science*, 2009, **49**, 60.
12 A. Smedberg, T. Hjertberg and B. Gustafsson, *Polymer*, 2004, **45**, 4867.
13 X. H. Zhang, H. M. Yang, Y. H. Song and Q. Zheng, *Polymer*, 2012, **53**, 3035.
14 A. L. Logothetis, *Progress in Polymer Science*, 1989, **14**, 251.
15 S. J. Oh and J. L. Koenig, *Journal of Polymer Science Part B-Polymer Physics*, 2000, **38**, 1417.
16 H. Azizi, J. Morshedian, M. Barikani and M. H. Wagner, *Advances in Polymer Technology*, 2011, **30**, 286.
17 H. G. Dikland, T. Ruardy, L. Vanderdoes and A. Bantjes, *Rubber Chemistry and Technology*, 1993, **66**, 693.
18 H. G. Dikland, L. Vanderdoes and A. Bantjes, *Rubber Chemistry and Technology*, 1993, **66**, 196.
19 Z. H. Murgic, J. Jelencic and L. Murgic, *Polymer Engineering and Science*, 1998, **38**, 689.
20 Y. Kawakami, Y. Kakihana, A. Miyazato, S. Tateyama and M. A. Hoque, *Silicon Polymers*, ed. A. M. Muzafarov, 2011, vol. 235, pp. 185.
21 G. Z. Li, L. C. Wang, H. L. Ni and C. U. Pittman, *Journal of Inorganic and Organometallic Polymers*, 2001, **11**, 123.
22 D. B. Cordes, P. D. Lickiss and F. Rataboul, *Chemical Reviews*, 2010, **110**, 2081.
23 L. Zhang, H. C. L. Abbenhuis, Q. H. Yang, Y. M. Wang, P. Magusin, B. Mezari, R. A. van Santen and C. Li, *Angewandte Chemie-International Edition*, 2007, **46**, 5003.
24 M. Joshi, B. S. Butola, G. Simon and N. Kukaleva, *Macromolecules*, 2006, **39**, 1839.

25 H. W. Milliman, H. Ishida and D. A. Schiraldi, *Macromolecules*, 2012, **45**, 4650.

26 K. Nusser, G. J. Schneider, W. Pyckhout-Hintzen and D. Richter, *Macromolecules*, 2011, **44**, 7820.

5 27 X. Wang, Y. Hu, L. Song, W. Y. Xing, H. D. Lu, P. Lv and G. X. Jie, *Journal of Polymer Research*, 2011, **18**, 721.

28 X. Y. Huang, L. Y. Xie, P. K. Jiang, G. L. Wang and Y. Yin, *European Polymer Journal*, 2009, **45**, 2172.

29 C. B. Cong, C. C. Cui, X. Y. Meng and Q. Zhou, *Journal of Applied* 10 *Polymer Science*, 2013, **130**, 1281.

30 D. Zhang, Y. Liu, Y. Shi and G. Huang, *RSC Advances*, 2014, **4**, 6275.

31 K. Zeng, L. Wang and S. X. Zheng, *Journal of Physical Chemistry B*, 2009, **113**, 11831.

15 32 J. F. Mu and S. X. Zheng, *Journal of Colloid and Interface Science*, 2007, **307**, 377.

33 L. Wang, K. Zeng and S. X. Zheng, *ACS Applied Materials & Interfaces*, 2011, **3**, 898.

34 Z. Y. Zhou, L. M. Cui, Y. Zhang, Y. X. Zhang and N. A. W. Yin, 20 *European Polymer Journal*, 2008, **44**, 3057.

35 Z. Y. Zhou, L. M. Cui, Y. Zhang, Y. X. Zhang and N. W. Yin, *Journal of Polymer Science Part B-Polymer Physics*, 2008, **46**, 1762.

36 Z. Y. Zhou, Y. Zhang, Z. Zeng and Y. X. Zhang, *Journal of Applied Polymer Science*, 2008, **110**, 3745.

25 37 Z. Y. Zhou, Y. Zhang, Y. X. Zhang and N. W. Yin, *Journal of Polymer Science Part B-Polymer Physics*, 2008, **46**, 526.

38 P. A. Agaskar, *Journal of the American Chemical Society*, 1989, **111**, 6858.

39 P. A. Agaskar, *Inorganic Chemistry*, 1991, **30**, 2707.

30 40 E. James, *Physical Properties of Polymers Handbook (Second Edition)*, Springer, Ohio, 2006.

41 J. D. Hoffman and R. L. Miller, *Polymer*, 1997, **38**, 3151.

42 X. H. Zhang, H. M. Yang, Y. H. Song and Q. Zheng, *Journal of Applied Polymer Science*, 2012, **126**, 939.

35 43 X. H. Zhang, H. M. Yang, Y. H. Song and Q. Zheng, *Journal of Applied Polymer Science*, 2012, **126**, 1885.

44 M. Lazar, A. Kleinova, A. Fiedlerova, I. Janigova and E. Borsig, *Journal of Polymer Science Part A-Polymer Chemistry*, 2004, **42**, 675.

40 45 J. C. Scanlan and H. H. Winter, *Macromolecules*, 1991, **24**, 47.

46 H. H. Winter, *Polymer Engineering and Science*, 1987, **27**, 1698.

47 H. H. Winter and F. Chambon, *Journal of Rheology*, 1986, **30**, 367.

48 H. P. Cong, P. Wang and S. H. Yu, *Small*, 2014, **10**, 448.

49 Y. C. Jung, N. G. Sahoo and J. W. Cho, *Macromolecular Rapid* 45 *Communications*, 2006, **27**, 126.

50 Y. Y. Shao, S. Zhang, M. H. Engelhard, G. S. Li, G. C. Shao, Y. Wang, J. Liu, I. A. Aksay and Y. H. Lin, *Journal of Materials Chemistry*, 2010, **20**, 7491.

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