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Reinforced Polyethylene/Clay Nanocomposites: Influence of Different Silane

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ABSTRACT

Montmorillonite (MMT) was first cation exchanged by cetyltrimethyl ammonium bromide (CTAB) and then treated by short chain silane (methyltrimethoxysilane) or different amount of long chain silane (dodecyltrimethoxysilane). High density polyethylene (HDPE)/clay nanocomposites were prepared through twin screw extruder using these silane modified clays without any compatibilizer. Thermal gravimetric analysis (TGA) proved the successful grafting of silanes onto clay. The effects of the chain length and content of the silanes on the dispersion state of clay and properties of the composites were studied using X-ray diffraction (XRD), transmission electron microscope (TEM), mechanical tests, creep tests and so on. The results indicate that the grafting of long chain silanes at higher content could improve the compatibility between clay and PE, thus more efficiently enhancing mechanical and creep properties of the composites than other silane treated clays.

Key Words: Polyethylene, Clay, Silane, Nanocomposites

1. INTRODUCTION

In recent years, polyethylene (PE)/clay nanocomposites have attracted a lot of academic and industrial interests because the addition of nano-scale dispersed clay has substantially improved the properties of the PE matrix, such as modulus, yield stress, stiffness, gas barrier, thermal stability and so on [1-8]. However, in order to obtain satisfactory properties from PE/clay composites, clay must be dispersed homogeneously into the polymer substrate. Clay exfoliation is one of the key issues which can determine the final properties of the composites.

There are two ways to delaminate clay into PE matrix. First one is in-situ polymerization method. Researchers have reported some exciting results using clay supported ethylene polymerization catalysts [9-11]. However, this method needs some sophisticated treatment of clay and is not favorable for large scale manufacture. The second one is melt compounding using neat PE. So far, melt compounding method is the most versatile and prevalent process in preparing PE/clay composites. For the melt compounding method, clay needs to be modified using organic compounds to improve its compatibility with PE and a certain kind of compatibilizer (such as maleic anhydride grafted PE, MA-PE) is usually added during compounding to facilitate the exfoliation of clay.

A lot of efforts have been dedicated to the synthesis and comparison of different clay modifiers and compatibilizers [12-18]. For example, Hotta *et al.* carefully studied the effects of the structures and amount of clay modifiers on the clay dispersion and mechanical properties of the composites [7]. The author concluded that organoclay having two long alkyl tails exhibited the best results. Osman and co-workers studied the properties of HDPE/clay composites containing different compatibilizers and pointed out that dispersion of the filler is essential in determine the

properties of the final products [12]. Lee *et al.* increased the modulus of HDPE by 67% using polyampholyte derivative of polyethylene (PE-g-PA, derived from melt compounding of MA-PE and 2-[2-(Dimethylamino)ethoxy]ethanol) as compatibilizer [13]. However, 50 wt% of this compatibilizer was needed to achieve such improvement.

On the other hand, the addition of compatibilizer can cause some problems. Usually, there are some high polarity groups on the compatibilizers. These groups may cause chain scission during the compounding step at high temperature and strong shear force. The compatibilizers could negatively affect the thermal stability of the composites [19, 20]. Also, the compatibility between these high-polarity compatibilizers and low-polarity PE matrix may still remain a problem [21]. Further, some kinds of clay modifiers and compatibilizers are difficult to synthesize, which is unsuitable for plant-scale manufacture.

So it is crucial to further improve the compatibility between clay and PE matrix by surface treatment of clay. It is well known that the inter layer cations of clay, such as Na^+ , Ca^{2+} , are readily to be exchange by organic ammoniums. Nearly all the reports published dealing with PE/clay nanocomposites have utilized this cation exchange reaction. But only cation exchange is not enough get a satisfactory degree of clay exfoliation. Fortunately, the silanol groups on the edge of clay layers are also potentially possible for further clay modification. This silanol groups can react with different silanes, thus improve the compatibility between clay and polymer matrix [22-26]. Some results have been reported dealing with the use of silane as clay modifier in the preparation of PE/clay nanocomposites. For example, Qian *et al.* prepared PE/clay composites using silane treated clay [24]. But the mechanical properties of the composites were not significantly improved though the matrix was LDPE and the elongation at break of the composite was only about 100%. Zhang and co-workers grafted silane groups onto clay and composites were made using this modified clay and PE [22]. However, the author didn't mention any mechanical properties of the composites. So, a systematic study on the silane structure and amount is still needed to clarify the best silane treatment parameters during the preparation of PE/clay nanocomposites.

In this paper, PE/clay nanocomposites are prepared using ammoniums and silane treated clay without any compatibilizer. Two kinds of silanes are used. One has a short carbon chain (methyltrimethoxysilane) and the other has a long chain (dodecyltrimethoxysilane). For the long chain silane, two amounts (high and low) are applied during clay treatment. The effects of different silane amount and silane chain length on clay dispersion state, crystallization behavior of the composites and mechanical properties of the composites are investigated. Creep behavior, which is very important to the long term properties of PE composites, is examined at a constant stress using DMA creep mode. There are only a few reports published dealing with the creep properties of PE/clay composites [27-30], so this study should be a complement for the present studies. High density PE (HDPE) was chosen as the polymer matrix since HDPE has been widely used and has much better mechanical properties than LDPE or LLDPE. So the incorporation of modified clay into HDPE should give us even better properties.

2. EXPERIMENTAL SECTION

2.1 Materials

Sodium montmorillonite (Na-MMT) used in experiments, with cation exchange capacity (CEC) of 90 mequiv/100 g, was obtained from Zhangjiakou Qinghe Chemical Factory. High density polyethylene (HDPE, HE3493) was kindly supplied by Borealis. Cetyltrimethyl ammonium bromide ($\text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_3\text{Br}^-$, AR, denoted as CTAB) was purchased from Beijing Chemical Reagent, China. Dodecyltrimethoxysilane ($\text{C}_{12}\text{H}_{25}\text{Si}(\text{OCH}_3)_3$, AR, denoted as C12 silane), methyltrimethoxysilane ($\text{CH}_3\text{Si}(\text{OCH}_3)_3$, AR, denoted as C1 silane), was obtained from Hubei Wuhan University Silicone New Materials. All reagents were used as received.

2.2 Surface modification of clay

The organophilic montmorillonite (organoclay, denoted as COMMT) was prepared via cation exchange reaction using CTAB alkylammonium. For this purpose, sodium montmorillonite (Na-MMT, 10 g) was dispersed in a ethanol/water mixture (100/100 vol/vol, 200 mL) by stirring at room temperature. Then CTAB (14.9 g, 120% of the CEC) was added to the clay suspension under stirring and the reaction mixture was stirred at 80 °C for 8 h. At the end of the reaction time, the suspension was filtered and the product was washed repeatedly with the mixture of ethanol/water.

Prior to the grafting reactions with clay, required amount of C12/C1 silane was firstly added into a 100 mL mixture of ethanol/water (90/10, v/v) to pre-hydrolyze for 1 h. The pH of the mixture solution was adjusted to 4 by addition of acetic acid. Then 10 g of COMMT was added into the mixture and the suspension was stirred vigorously at 80 °C for 24 h. The products were filtered and washed by mixture of ethanol/water. The silane-modified clay products were denoted as C12HMMT, C12LMMT, C1MMT, corresponding to high concentration of C12 silane (0.92 mmol of C12 silane/1g of MMT), low concentration of C12 silane (0.17 mmol of C12 silane/1g of MMT), and C1 silane (0.74 mmol of C1 silane/1g of MMT), respectively. All the clay samples were dried at 80 °C for 48 h in a vacuum, ground into powder, and sifted through a 300-mesh sieve.

2.3 Preparation of PE/clay composites

The nanocomposites of different clay contents (3, 6, 10 wt%) were prepared by premixing HDPE and clay samples and then melt compounding in a HAAKE Mini Extruder using the counter rotation mode under the protection of dry nitrogen. The screw speed was 80 rpm, compounding time and temperature were 9 min and 190 °C respectively. The composites were named as PE/COMMT, PE/C1MMT, PE/C12LMMT and PE/C12HMMT respectively according to the different clays used in the compounding step. The obtained materials were hot pressed into films with a thickness of about 0.2 mm using Hot Press. The temperature of the hot press was set at 190 °C, and the pressure was 8000 Psi. After the pressure reached the designated value, the pressure was held for 4 min and then released. The composite films were taken out and quenched in room temperature at about 25 °C. The film was cut to a dog bone shape for mechanical tests. The gauche length was 9.53 mm, width was 3.18 mm. For the DMA creep tests, the film was cut to a rectangular shape with a length of about 15 mm, width of about 5 mm and thickness of about 0.2 mm. Also, the DSC, XRD, and TEM samples were all taken from the films.

2.4 Characterization

The thermal gravimetric analysis (TGA) was performed on a TA Q-500 series analyzer with a heating rate of 20 °C/min in nitrogen atmospheres from 50 °C to 700 °C. XRD curves were obtained using a Rigaku D/max 2400 diffractometer with Cu K_α radiation ($\lambda=0.154$ nm, 40 kV, 120 mA) at room temperature. The scanning 2θ range was from 1° to 40°. A TA Q10 differential scanning calorimeter (DSC) thermal analyzer was used for DSC analysis. Sample weight was about 3 mg and tests were under the protection of dry nitrogen. The DSC sample was first heated from 50 °C to 190 °C at a heating rate of 10 °C/min and kept at 190 °C for 5 min. Then the sample was cooled to 50 °C at a cooling rate of 10 °C/min. The heat diffusion during DSC tests was normalized according to the polymer content of the sample. TEM was carried out on Hitachi (Japan) H-800 microscope at an acceleration voltage of 100 kV. Mechanical properties of the composites were obtained using the Instron Microtester 5848 at about 25 °C with the load cell of 50 N, the

crosshead speed was 50 mm/min. Creep tests were done using a TA-Q800 Dynamic mechanical Analyzer using creep mode. The temperature was 35 °C and the stress was set at 5MPa or 10 MPa.

3. RESULTS AND DISCUSSION

3.1 TGA results

The TGA curves of Na⁺-MMT, C0MMT, and the silane-treated organo-clay are shown in Figure 1. The silane contents of different kinds of clays are calculated from the TGA data and summarized in Table 1. All the modified clays start to decompose at about 250 °C, well above the PE processing temperature using in this study. So during the compounding of the composites, the modifiers will not decompose. The organic component of C0MMT is about 40 wt% according to TGA curves. Silanes were successfully attached onto clay layers based on TGA results. The weight remaining percentage of silane-treated clays decreases compared to that of C0MMT, which means higher organic contents. The weight percentage of silanes in different clays varies according to different kinds and amounts of silanes used during the treatment of clay (details were listed in Table 1). For example, the silane weight percentage is 9.4 wt% for C12HMMT; while the value is 4.6 wt% for C12LMMT. So, the structure and amount of silanes located on the clays could be controlled in the present synthesis method.

Figure 1. TGA curves of the clays

Table 1. Silane contents of the clays

Clay	Silane wt%
C1MMT	2.6
C12LMMT	4.6
C12HMMT	9.4

3.2 Interlayer spacing of the clays

XRD results represent the inter-layer distance of the clays. For the pristine clay (Na⁺-MMT), the d(001) peak appears at $2\theta \approx 7.2^\circ$, the corresponding basal spacing is 1.23 nm. After the treatment of alkylammoniums, the d(001) peak of C0MMT moves toward lower angle, at about 4.55 degrees. This indicates that Na⁺ has been exchanged by

alkylammoniums and the inter-layer distance of the clay had been expanded to about 1.94 nm. However, further treatment by different silanes doesn't have any obvious effects on the gallery spacing of clays. For example, the d(001) peak of C12HMMT shows at about 4.60 degrees, very close to the value of COMMT. This phenomenon seems reasonable. Since the silanes are supposed to be located mainly on the edge of clay platelets, where silanol groups exist [25], the silanes are unlikely to enter the inter-layer space of COMMT, further enlarging the inter-layer distance. The diffraction peaks of the silane treated clays remain strong and sharp, so the layered structure is not destroyed by the silanes.

Figure 2. XRD curves of the clays

3.3 Dispersion of clay

X-ray diffraction is by-far the simplest way to examine the dispersion state of the clay layers in polymer substrate. The XRD curves of the PE/clay composites are summarized in Figure 3 and Figure 4. In Figure 3, the XRD curves of the composites containing 6 wt% different kinds of clays are put together for compare. While in Figure 4, the XRD data of PE/C12HMMT composites at different clay contents is shown.

Figure 3. XRD curves of the composites containing 6 wt% of different clays

First of all, according to Figure 3, the diffraction peaks of the composites in which the clays were further treated by silanes appear at lower angles than that of PE/C0MMT. So silanes were effective in improving the dispersion of clay in this study. It is obvious that the clay in PE/C12HMMT composite has the largest interlayer spacing among all the clays. This should be ascribed to the fact that C12HMMT had the largest amount of silane chains that attached to the surface of organo-clay. The compatibility between C12HMMT and PE should be better than other clays. This made it easier for the PE chain to diffuse into the gallery of clay and facilitated the exfoliation of clay under strong shear force during compounding. For the case of PE/C12LMMT and PE/C1MMT, the peaks of the corresponding XRD patterns appear close to each other, at higher angles compared with that of PE/C12HMMT. For example, the diffraction peak of PE/C1MMT is at 2.30 degrees, corresponding to the interlayer distance of 3.84 nm; while for PE/C12HMMT, the peak appears at 2.15 degrees, the gallery spacing was 4.10 nm. Though for C12LMMT, the silane has a much longer carbon chain length than C1MMT, the amount of C12 silane is not enough to further improve the dispersion of clay. This indicated that for C1MMT and C12LMMT, the polarity of the two kinds of organoclay is still too high.

Figure 4. XRD curves of the composites containing different amount of C12HMMT

The contents of clay in the composites also have some effects on the dispersion of clay. Based on Figure 4, as the C12HMMT content increases for the composites, the diffraction peaks move toward higher angle, which means smaller interlayer spacing of the clay. So, although the silanes could improve the compatibility between clay and PE, complete compatibility of the two hasn't been achieved yet.

Figure 5: TEM images of the composites, A) PE/C0MMT, B) PE/C1MMT, C) PE/C12LMMT, D) PE/C12HMMT. (Clay contents: 6 wt%)

TEM can give us a direct insight into the dispersion of clay. The TEM images of the composites agree well with XRD results. For PE/C0MMT, at low magnification, micro-meter size of clay agglomerates can be observed, the dispersion of clay is far from homogeneous. For PE/C1MMT and PE/C12LMMT, dispersion of clay is improved a little. Big grains of clay couldn't be observed. However, clay dispersion can only be considered as intercalated, the size of clay platelets is around 100-200 nm. Satisfactory dispersion of clay could be obtained when clay was treated by high content of long chain silane. Clearly, for PE/C12HMMT, at low magnification, no clay aggregates are observed, homogeneity of clay is good. At high magnification, the particle size is around 30 nm, clay is partially exfoliated and partially intercalated. As a conclusion for the clay dispersion, silane treatment is important to improve the dispersion state of clay. High content of long chain silane could provide better results.

3.4 DSC results

Crystallization behavior is very important to the mechanical properties of a semi-crystalline polymer, such as PE. DSC studies of the composites were carried out to determine the effects of clays on the crystallization of the composites.

DSC heating and cooling curves of pure PE composites containing 6 wt% of different clays are compiled together in Figure 6. The melting (T_m), crystallization (T_c) temperatures and crystallinities of the composites calculated from the heating curves are listed in Table 2. The percentage of crystallinity is estimated using a value of heat of fusion of 293 J/g for 100% crystalline PE according to published results [31].

Table 2. DSC results of the composites containing 6 wt% of clay

Sample	T_m (°C)	T_c (°C)	Crystallinity (%)
Pure PE	128.5	117.3	59.2
PE/C0MMT	127.9	118.7	60.6
PE/C1MMT	128.1	118.5	60.5
PE/C12LMMT	128.3	117.9	59.3
PE/C12HMMT	128.2	117.7	59.1

Figure 6. DSC curves of the composites containing 6 wt% of clay. Left: heating curves. Right: cooling curves.

Clearly, clay has an ability to initiate the crystallization of PE matrix. For the DSC cooling curves, these PE/clay composites have higher T_c than pure PE. However, different clays have different nucleating effects. PE/C0MMT has the highest T_c and crystallinity, while silane treated clay gives the composites lower crystallization temperatures. Here, the chain length of the silanes seems to be more effective in reducing the nucleating ability of clay. The T_c and crystallinity of PE/C1MMT are still close to PE/C0MMT, 118.5 °C and 60.5% respectively. However, the crystallinity of PE/C12LMMT is 1.3% lower than PE/C0MMT. When C12 silane amount is further increased, it is evident that C12HMMT had the weakest nucleating ability. First, C12HMMT had lower pristine clay content according to TGA results; second, when clay was covered by organic compounds, the nucleating ability would be weakened [32, 33]. The crystallinities of the composites gave the same results. The crystallinity of PE/C12HMMT is 59.1%, while for PE/C0MMT, the value is 60.6%.

As discussed above, high amount of long chain silane has a negative effect on the nucleating ability on clay, which is not good for the mechanical properties of the material. However, homogeneous dispersion and better interfacial properties may compensate this disadvantage for PE/C12HMMT. On the other hand, the crystallinity of PE/C12HMMT is not increased compared to pure PE, which is positive for the composite to retain the value of elongation at break.

3.5 Mechanical Properties

The typical strain-stress curves of the composites containing 6 wt% of different kinds of clay are shown in Figure 7. The elongation at break is not included in Figure 7 since the value is quite large. Young's modulus, yield stress and elongation at break of all the composites are summarized in Table 3.

Figure 7. Typical strain-stress curves of the composites containing 6 wt% of clay

Clearly, the shapes of the strain-stress curves in Figure 7 are similar. However, the initial slopes of the curves and tensile yield points varied according to different kinds of clay, which means different Young's modulus and yield stress. So clay modification is crucial in determining the mechanical properties of PE/clay composites. As listed in Table 3, all the composites have higher modulus than pure PE regardless of clay contents and treatment. The clay particles dispersed in PE matrix must have a strong effect in retarding the small scale movement of PE chain and PE spherulites. For nearly all the samples, modulus increased with the increasing of clay contents. More clay platelets would have a stronger effect in restraining PE chains.

The modification of clay substantially influenced the values of modulus. For C0MMT without further treatment of silane, the modulus of the corresponding composite is increased by only 14% at 6 wt% of clay. When C0MMT was treated by short chain silane or low content of long chain silane, the increase of modulus is about 16-17% (6 wt% of clay). For Young's modulus, there seems to be no big difference for PE/C1MMT and PE/C12LMMT. Since the modulus is calculated when the strain of the composite sample is very small, the dispersion of clay should be the key issue while the interfacial property will be secondary. And based on XRD and TEM results, the homogeneity of clay in these two composites is almost the same. So these two composites have almost the same value of Young's modulus.

However, for PE/C12HMMT, the corresponding composite had a modulus of 25% higher than that of pure PE at 10 wt% clay. Obviously, C12HMMT has a much more homogeneous dispersion state in PE matrix than the other clays according to TEM and XRD results. So, the "density" of clay layers within PE matrix will be higher for C12HMMT though the inorganic content of C12HMMT is the lowest among all the clays in this study. These well-dispersed silicate layers can retard the small movement of PE chains when a stress is exerted on the composite at the initial state of mechanical tests, increasing the modulus more efficiently than other clays. Even though composites containing C12HMMT has lower crystallinities than other composites at the same clay content, the corresponding modulus is higher due to the reinforcing effect of exfoliated clay layers.

For yield stress, the influence of clay treatment is more prominent. When clay was not further treated by silanes or only treated by C1 silane, the interfacial properties must be poor, there was hardly any interaction between filler and

matrix. For example, the yield stress of PE/C0MMT is 21.7 MPa at 6 wt% of clay, lower than 22.2 MPa, which was the yield stress of pure PE. As the clay contents of C0MMT and C1MMT increase, the yield stress even got worse. So, there is no stress-transfer mechanism in these composites. The filler might actually act as craves or flaws in the composites. When composite sample is deformed, the load force couldn't be transferred to the rigid filler. However, these fillers might even initiate cracks within the composites. As shown in Table 3, the elongation at break of these composites is much lower than pure PE and PE/C12HMMT. For PE/C12LMMT, the situation is a little better. The yield stress is higher than pure PE but the increase is not prominent. The long silane chain should have some opportunity to entangle with PE chains, introducing some stress transfer mechanism to increase the yield stress value, but this effect is not strong enough.

Table 3. Mechanical properties of the composites

Sample	Clay content (wt%)	Young's Modulus (MPa)	Yield Stress (MPa)	Elongation at Break (%)
Pure PE	0	436 ± 10	22.2 ± 1.0	1400±150
PE/C0MMT	3	478 ± 12(+10%)	21.9 ± 0.8(-1%)	521±216
	6	498 ± 23(+14%)	21.7 ± 1.3 (-2%)	379±92
	10	503 ± 27(+15%)	21.1 ± 1.5 (-5%)	276±136
PE/C1MMT	3	495 ± 17(+13%)	22.5 ± 0.6(+1%)	803±133
	6	507 ± 11(+16%)	22.2 ± 1.3(+0%)	420±87
	10	519 ± 14 (+19%)	21.4 ± 1.3(-4%)	367±98
PE/C12LMMT	3	490 ± 13 (+12%)	22.7 ± 0.9(+2%)	735±128
	6	512 ± 20 (+17%)	22.8 ± 0.9(+3%)	550±96
	10	512 ± 18 (+17%)	22.7 ± 1.1(+2%)	433±122
PE/C12HMMT	3	510 ± 8 (+17%)	23.2± 1.6 (+5%)	1390±260
	6	528 ± 19 (+21%)	24.7 ± 0.6 (+11%)	1295±165
	10	540 ± 13 (+25%)	23.8 ±0.8 (+7%)	1020±230

When organo-clay was treated with high content of long chain silanes, the clay dispersion and interfacial properties must be better. The stress exerted on the composite sample could be transferred to clay layers, to some extent. For example, when C12HMMT content is 6 wt%, yield stress of PE/C12HMMT is increased by 2.5 MPa compared to pure PE. When clay content was further increased to 10 wt%, yield stress decreases to about 23.8 MPa. This should be due to the fact that the homogeneity of clay was not good at high clay content, as confirmed by XRD results. However, the elongation at break of PE/C12HMMT nanocomposites is satisfactory, close to that of pure PE. Usually, the reinforcing effect would be accompanied by much lower value of elongation at break. But this phenomenon was not observed in our study because the interfacial properties is improved by silanes and the modified filler would not be so effective in initiating crack during tensile tests. In the range of our study, the best clay content for PE/C12HMMT appears at 6 wt%. At 3 wt%, clay content is too low to show substantial reinforcing effect. When clay content is higher than 6 wt%, the mechanical properties of the composites start getting worse due to homogeneity issue.

3.6 Creep properties

Creep tests were first performed on DMA at a given stress of 5 MPa. The strain after 1 hr of displacement and strain after 30 min of recovery are taken into consideration to evaluate the ability of the composites to resist shape change when a force is exerted. Creep behavior is very important since PE/clay composites were usually considered as structural materials and would be used under certain stress for a long time.

Figure 8. Typical creep curves of the composites containing 6 wt% of clay (static force is 5 MPa)

Typical creep curves are shown in Figure 8 and the strain values calculated from these curves are listed in Table 4. Clearly, for all the samples, when the static force is applied, there is a sudden “jump” in the strain. As creep tests go on, the slope of the curve gets smaller, and almost flat after 1 hr. However, if C0MMT was added into PE matrix, the creep properties would get worse. Both strain after displacement and strain after recovery are increased. For example, at 6 wt% of clay, the strain after displacement and recovery are increased by 21% and 31%, respectively. So, in this case, clay has no effect on retarding the movement of PE chain. However, due to inhomogeneous dispersion of clay and poor filler-matrix interfacial properties, C0MMT could cause stress concentration and initiate cracks, the strain after displacement and irrecoverable strain were even higher than pure PE. When clay is treated by C1-silane or low content of C12-silane, the situation is a little better. But the strain values are quite close to pure PE. The compatibility between clay and PE could be improved a little using C1-silane or low content of C12-silane, however, the dispersion of clay and interfacial properties are not substantially improved.

Table 4. Creep results of the composites (5 MPa)

Sample	Clay Content (wt%)	Strain after 1 hr Displacement	Strain after 30 min recovery
Pure PE	0	4.2	1.6
PE/C0MMT	6	5.1 (+21%)	2.1 (+31%)
PE/C1MMT	6	4.1 (-2%)	1.4 (-12%)
PE/C12LMMT	6	3.9 (-7%)	1.3 (-19%)
PE/C12HMMT	3	3.5 (-17%)	1.0 (-37%)
	6	3.2 (-24%)	0.8 (-50%)
	10	2.9 (-31%)	0.8 (-50%)

On the other hand, high content of C12-silane treatment was effective to improve the creep properties of the composites. After the addition of C12HMMT, the jump at the initial state was decreased. The strain at 1 min of displacement is reduced by about 30%. The well dispersed clay layers could impede the movement of PE chain, so the slope of the creep curves for the composites containing C12HMMT will get smaller faster than pure PE, resulting in a smaller strain after 1 hr of displacement. The creep strain can be reduced by over 30% for the PE/C12HMMT composites. Though all the samples displayed permanent irrecoverable strain after 30 min of recovery, PE/C12HMMT composites had smaller strains after recovery than pure PE and PE/C0MMT composites. This is to say, PE/C12HMMT had a more elastic behavior under stress, which is favorable in daily usage. As seen from the Table 4, the strain after 30 min recovery can be reduced to half the value of pure PE, this is a substantial enhancement.

The creep behavior of PE/C12HMMT under higher stress (10 MPa) is also studied. The stress applied is almost half the value of yield stress. The composites of PE/C12HMMT perform well in the tests. The values of strain after displacement and recovery are greatly reduced, just like the creep tests under 5 MPa stress. At 10 wt% of clay, the strain after displacement and recovery can be reduced by almost 30%.

Figure 9. Typical creep curves of the composites containing C12HMMT (static force is 10 MPa)

Table 5. Creep results of the composites (10MPa)

Sample	Clay Content (wt%)	Strain after 1 hr Displacement	Strain after 30 min recovery
Pure PE	0	21.9	9.3
PE/C12HMMT	3	18.9 (-14%)	7.5 (-19%)
	6	16.3 (-26%)	7.1 (-24%)
	10	15.5 (-29%)	6.7 (-28%)

4. CONCLUSIONS

In this study, ammonium treated clay was further treated by short chain silane and long chain silane at different amount. PE/clay composites were prepared using these silane treated clays without any compatibilizer. The properties of the composites were compared according to different silane treatment. Clays treated by higher amount of long chain silane had better dispersion state based on XRD and TEM study. Though clay treated by short chain silane and low content of long chain silane had stronger abilities to initiate the crystallization of PE, PE composites containing clay treated by high content of long chain silane had much better mechanical and creep properties due to homogenous clay dispersion and better interfacial properties. Further, the elongation at break of PE/C12HMMT at different clay contents was close to that of pure PE. So, as a conclusion, silanes were effective in modification of clay. High content of long chain was needed to improve the compatibility between clay and PE matrix, providing better properties.

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