Dynamic Rheological Behavior and Mechanical Properties of PVC/CPE/MAP-POSS Nanocomposites

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ABSTRACT: Poly(vinyl chloride)/chlorinated polyethylene (PVC/CPE)/methylacryloylpropyl-containing polyhedral oligomeric silsesquioxane (MAP–POSS) nanocomposites are prepared. The plastic behavior and dynamic rheological behavior of PVC/CPE/ MAP–POSS are investigated. The influences of composition on dynamic storage modulus *G'*, loss modulus *G''*, and complex viscosity η^* of PVC/CPE/MAP–POSS melts are discussed. The dynamic mechanical properties, mechanical properties, and morphology are determined. The results show that both plastic time and balance torque of the nanocomposites decrease, but the *G'*, *G''*, and η^* all increase with increasing MAP–POSS content. The maximum value of the dynamic mechanical loss tan δ decreases and elasticity increases when MAP–POSS is added. The impact strength of the nanocomposites increases with increasing MAP–POSS content and has the best value at 10% content of MAP–POSS, which is 5.38 kJ/m² higher than that of the blend without MAP–POSS. The MAP–POSS can be used as an efficient process aid and impact aid for the PVC/CPE blend. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 174–180, 2013

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INTRODUCTION

Poly(vinyl chloride) (PVC) is used for the manufacturing of a wide range of products with different properties at relatively low cost. However, the utilization of PVC is restricted by the poor thermal and mechanical properties.^{1–3} Many efforts have been made to improve the toughness of PVC. Chlorinated poly-ethylene (CPE) is the most commonly used modifiers of the PVC, and the properties of the PVC/CPE blends have been studied widely.^{4–10}

Polyhedral oligomeric silsesquioxane (POSS) has been shown to have great potential in the synthesis of organic/inorganic hybridized materials and thus has attracted much attention in the recent years.^{11,12} The typical T_8 POSS monomers possess the structure of a cube-octameric framework with eight organic corner groups. The diversity of organic groups on POSS cage can provide one with tremendous space for maneuver to control the microstructure of POSS.¹³ These organic function groups make the POSS nanostructure compatible with many polymers or monomers. POSS is usually used as a modifier or reinforcer of polymeric materials. Compared to other modifiers, its special cage structure and good compatibility with polymer can make modified effect qualitative leap. These enhancements have shown to apply to a wide range of thermoplastic and thermosetting systems.^{13,14} Soong et al.¹² had studied the plasticizing effect of methylacryloylpropyl–POSS (MAP–POSS) to PVC. The results showed that the PVC was further plasticized with increasing MAP–POSS content.

To the best of our knowledge, the dynamic rheological behavior, plastic behavior, and dynamic mechanical properties of the PVC/CPE/MAP-POSS nanocomposites have been rarely studied. In this work, the PVC/CPE/MAP-POSS nanocomposites are prepared, and the plastic behavior and dynamic rheological behavior are investigated. The influences of MAP-POSS content on storage modulus G', loss modulus G', complex viscosity η^* , and stress relaxation are discussed; the dynamic mechanical properties, mechanical properties, and morphology of the PVC/ CPE/MAP-POSS nanocomposites are also characterized. The dynamic rheological behavior shows that the storage modulus E' and loss modulus E'' of nanocomposites both increase with increasing MAP-POSS content and has the best impact strength at 10% content of MAP-POSS, which is 5.38 kJ/m² higher than that of the pure PVC/CPE blend at the same CPE content. The MAP-POSS can be used as an efficient process aid and impact aid of the PVC/CPE blend.

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Scheme 1. The structures of methylacryloylpropyl–POSS T_8 and T_{10} .

EXPERIMENTAL

Materials

Polyvinyl chloride (DG-1000K) was supplied by Dagu Chemical, China. CPE (135A) with a chlovine content of 35 wt % was supplied by Jingxin Chemical, China. The methylacryloylpropyltrimethoxysilane (MAPTMS), chemical pure grade, was supplied by Shenda Chem., Beijing, China. The tribasic lead sulfate (TLS), dibasic lead phosphite (DLP), zinc stearate (ZS), wax, dibutyl phthalate (DBP), and tetramethylammonium hydroxide (TMAH) are all of commercial grade and were supplied by Beijing Chem Reagent, China. The MAP-POSS was synthesized by the hydrolytic reaction of MPTMS catalyzed with TMAH according to Refs. ¹³ and ¹⁵. The yield is 85 wt %, and the liquid chromatography/mass spectrometry (Agilent 1100, Agilent, USA) was used for the determination of the components of MAP-POSS and the detailed structure. The result shows that T_8 is the main product and some amount of T_{10} contained, and the structures were shown in Scheme 1.

Preparation of PVC/CPE/MAP-POSS

Nanocomposites Samples

Ten samples of blends were prepared, and the compositions of PVC/CPE and PVC/CPE/MAP–POSS were shown in Table I. The PVC/CPE and PVC/CPE/MAP–POSS blends were marked as C0, C5, C10, C15, C20, C10M0, C10M3, C10M5, C10M7, and C10M10, respectively. Then, 3 g TLS, 2 g DLP, 1.5 g ZS, 0.5 g wax, and 10 mL DBP were added to the mixture mentioned earlier, respectively. All components were first mixed in a mixer and then milled on a laboratory two-roll mill at 185°C. The 5-mm and 1-mm-thick plates were pressed at 180°C and then cold-pressed for 10 min at 5 MPa in order to determine

Table I. The Composition of Blends

dynamic rheological behavior, dynamic mechanical properties, and mechanical properties.

Determination of Plastic and Dynamic Rheological Behavior

The plastic behavior of PVC/CPE/MAP–POSS nanocomposites was investigated at 185°C using a torque rheometer (Shanghai Kechuang, XSS-300, China). Dynamic rheological measurements were performed using an oscillation rheometer (AR2000ex, TA, USA) equipped with a parallel plates of 25 mm in diameter at 185°C, the frequency ranges from 0.1 to 100 Hz, and strain at 1.25%. Storage modulus (*G*'), loss modulus (*G*'), and complex viscosity (η^*) of melts were measured in the frequency scanning experiments. Stress-relaxation behavior was measured at 185°C and strain at 10%.

Determination of Dynamic Mechanical Properties

Dynamic mechanical properties of PVC/CPE/MAP–POSS nanocomposites were investigated using a dynamic mechanical analyzer (DMA-8000, Perkin Elmer, USA). The sample size was 20 × 5 × 0.8 mm. Heating rate was 2°C/min, and the frequency was 2 Hz. The range of testing temperature was from -80 to 150°C.

Determination of Mechanical Properties and Morphology

Tensile strength test was performed using an electronic tensile tester (WSM-20 kN, Changchun Tester, China). Tests were conducted at an extension rate of 20.0 mm/min at 25° C and 50% relative humidity. The notch impact test was carried out on an impact tester (XCJ-40, Chengde Tester, China).

The morphological structure of nanocomposites for zone of fracture was investigated by scanning electron microscopy (SEM; KYKY-2800B, KYKY, China).

RESULTS AND DISCUSSION

Mechanical Properties of PVC/CPE/MAP-POSS Nanocomposites

Table II shows the data of impact and tensile strength of samples. As seen from Table II, the impact strength of PVC/CPE blends increases with increasing CPE content, but tensile strength decreases with increasing CPE content. The impact strength of C20 is 24.33 kJ/m² higher than that of C0. But, in practiced industry, the CPE content in PVC/CPE blend is not higher than 10 wt %.

For PVC/CPE/MAP–POSS nanocomposites, the impact strength increased, but tensile strength decreased with increasing MAP–POSS content. The nanocomposite has the best impact strength at 10% content of MAP–POSS (C10M10), and it is 5.38 kJ/m^2 higher than that of C10M0. The MAP–POSS can enhance the

Sample no.	CO	C5	C10	C15	C20
PVC (g)	100	95	90	85	80
CPE (g)	0	5	10	15	20
Sample no.	C10M0	C10M3	C10M5	C10M7	C10M10
PVC (g)	90	90	90	90	90
CPE (g)	10	10	10	10	10
MAP-POSS (g)	0	3	5	7	10



Sample no.	CO	C5	C10	C15	C20
Impact strength (kJ/m ²)	2.04	3.86	6.90	11.45	26.37
Tensile strength (MPa)	23.48	22.45	20.36	19.02	16.84
Sample no.	C10M0	C10M3	C10M5	C10M7	C10M10
Impact strength (kJ/m²)	6.90	8.01	8.91	11.42	12.28
Tensile strength (MPa)	20.36	14.28	11.58	10.44	9.55

Table II. Data of Impact Strength and Tensile Strength of Blends

impact strength of PVC/CPE blends as an impact aid, but it has some action to decrease tension strength.

Figure 1 shows the SEM photographs of impact-fractured surface of C10M0 and C10M7. As seen from Figure 1, the fracture behavior of C10M0 shows some toughness characteristics, and it is due to the enhancement of CPE to PVC. Fracture surface of C10M7 is not so clear-even and appear some layer structure. The toughness of C10M7 is obviously better than that of C10M0, and it is due to the toughing effect of MAP–POSS.

Plasticizing Behavior of PVC/CPE/MAP-POSS Melts

Relationship among the balance torque, plastic time, and MAP-POSS content is shown in Figure 2. As seen from Figure 2, the balance torque of the nanocomposites and plastic time both decrease with increasing MAP-POSS content. When MAP-POSS content is 10 wt %, the balance torque and plastic time are 0.5 $\mathrm{N^*m}$ and 81 s decreased than that of pure PVC/CPE blend, respectively. In the plasticizing process, the PVC resin was broken into primary particles and then turned into much smaller particles until the end of plasticizing process at high temperature and constant mechanical stirring.¹⁶ MAP-POSS has a much less volatile, lower viscosity, and an organic/inorganic-hybridized structure. In the mixture, the MAP-POSS has a lower melting point, and the MAP-POSS molecule, which is equivalent to nanometer particles, will fill into free volume between PVC and CPE molecule chains. It is suggested that MAP-POSS has plasticizing effect and lubrication in the melt. Thus, the balance torque and plastic time of the nanocomposites both decrease with increasing MAP-POSS content. MAP-POSS can also be used as a processing aid for PVC/CPE blend.

Dynamic Rheological Behavior of PVC/CPE/MAP–POSS Melts Rheological tests are sensitive due to molecule chain entanglements or chain structure such as small differences in chain length, branching, or networking. These factors will cause a large variation in flow behavior.¹⁷ In the polymer processing, a clear and accurate understanding for the rheological properties of various polymers or polymer composites is important. Rheological behavior can provide information on the internal structure of materials and should be controlled for industrial applications. It is known that the storage modulus G' of melts is more sensitive than the loss modulus G'' to morphology or rheological properties of the materials in the rheological experiment, because storage energy G' between molecules is more related to rheological properties of melts than that of energy loss G''.^{17,18}

The dynamic storage modulus G' is related to the elastic behavior of the material; the dynamic loss modulus G'' represents the dissipated energy.^{19,20} The dependence of G' and G'' on the frequency can measure the relative motion of molecules in the bulk and can also give important information about the flow behavior of melts. The increase in elastic modulus may result from the change in molecular chain rigidity and the interaction between polymer chains. Figures 3 and 4 show the logarithmic plots of G' versus and G'' versus frequency (Hz) of PVC/CPE/ MAP–POSS nanocomposites at 185°C, respectively. As seen from Figures 3 and 4, the G' and G'' of nanocomposite melts both exhibit a monotonic changing with frequencies and both increase with increasing MAP–POSS content, but they are all lower than that of pure PVC/CPE blend (C10M0).

Larson²¹ has demonstrated that the G' and G'' are solid-like and liquid-like material behaviors, respectively. For the liquid-like behavior, the G' is much lower than the G'' and vice versa for the solid-like system. In this work, all samples behave as visco-elastic solid, and because G' > G'' at any frequency, the elastic response is similar to solid material.

Solid-like behavior has been observed in conventional filled polymer systems, in which strong interactions exist among the polymers and the fillers.^{22,23} It is suggested that the MAP–POSS molecule, which is equivalent to nanometer particles, will fill



Figure 1. SEM photographs of impact breaking surface of C10M0 and C10M7.



Figure 2. The relationship among the balance torque, plastic time, and MAP–POSS content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

into free volume between PVC and CPE molecule chains. It has a plasticizing effect and lubrication on molecular movement. When a small amount of MAP-POSS is added, the movement of PVC and CPE segments will become easier than that of the melt without MAP-POSS. Thus, G' and G'' of C10M3 are lower than that of C10M0. But the oxygen atom of carbonyl group on MAP-POSS can form weak hydrogen bond with -HCCl- on PVC and CPE molecules. Moreover, methylacryloylpropyl group of the MAP-POSS can form free group at high temperature and react with PVC and CPE molecules or vinyl group formed by dehydrochlorination of PVC and CPE molecules. Thus, with increasing MAP-POSS content, more MAP-POSS will be adsorbed or reacted to PVC and CPE molecular chains, and some kind of "network structure" will be formed.¹⁸ The interactions among the polymers and MAP-POSS molecules (the fillers) will be enhanced. The free rotation and movement of molecular chains were capably restricted and prevented the complete relaxation due to physical or chemical jamming; thus, G' and G'' increase with increasing MAP–POSS content.



Figure 3. Relationship between G' and frequency of PVC/CPE/MAP–POSS melts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 4. Relationship between G'' and frequency of PVC/CPE/MAP–POSS melts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 shows the plots of complex viscosity η^* versus MAP– POSS content. As seen from Figure 5, the η^* of PVC/CPE/ MAP–POSS melts exhibits a monotonic decrease with the increasing frequency, but the η^* increases with increasing MAP– POSS content. However, all η^* of melts are lower than that of C10M0. This is similar to changes of G' and G'' as discussed earlier. It demonstrates that the friction force between the molecules will be decreased when a small amount of MAP–POSS is added and will lead to η^* of the melts decrease. The network structure will be formed as a result of increasing MAP–POSS content (physical and chemical, because the some cross reaction can be formed between MAP–POSS, PVC and CPE); thus, the friction force between the molecules will be increased, and η^* of the melts will be increased.

Figure 6 shows the stress relaxation of melts. As seen from Figure 6, when the MAP-POSS content increases, the shear



Figure 5. Relationship between η^* and frequency of PVC/CPE/MAP–POSS melts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 6. Stress relaxation of PVC/CPE/MAP-POSS nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stress of melts increases and also delays the time to reach the final equilibrium stress; however, the relaxation curve of C10M3 is still below all the curves of PVC/CPE/MAP–POSS melts. It also shows that when a small amount of MAP–POSS (3 wt %) is added to the PVC/CPE matrix, the plasticizing effect and lubrication of MAP–POSS play a main role. Therefore, the free rotation of chain segments becomes easier, less time is needed to achieve relaxation of the molecule chain, and the melt will have a weak elastic response. If the MAP–POSS content continues to increase, more MAP–POSS will be adsorbed to polymer molecular chains (or reaction with it). The segment movement will become more difficult; then the elasticity of melts increases and the relaxation time will be longer. This is consistent with the dynamic rheological behavior, as discussed earlier.

Dynamic Mechanical Properties of PVC/CPE/MAP-POSS

Dynamic mechanical analysis is a molecular level analysis method reflecting the interaction and movement of molecules. Under the action of alternating stress, the mechanical energy is used to change the molecular chain conformation. When the molecular chain stretches, the energy is stored as elastic potential energy; when the molecular chains huddle up, overcoming the intermolecular friction force is required. At that time, the potential energy turns into heat energy and then dissipated. Meanwhile, dynamic mechanical analysis (DMA) can also be described as an effective method for determining the interaction on a molecular level between the different components in the materials.²⁴

In DMA experiment, the mechanical loss tan δ peak temperature T_p reflects the micro-Brownian movement of polymer segment. Generally, there is a one-to-one relationship between the glass transition temperature T_g and T_p ; the T_p is often designated as T_g , and the higher the T_p , the higher the T_g is, which depends on the molecular chain structure and material morphology. DMA was determined from -80 to 150° C, and the relationship between tan δ and temperature T is shown in Figure 6. The curves are all very flat from -80 to 40° C. This is because there is only 10 wt % CPE added in the samples, and **Applied Polymer**

so the mechanical loss tan δ peak of CPE is not obvious at low temperature.

As seen from Figure 7, there is only one mechanical loss peak of each curve; thus, MAP-POSS, CPE, and PVC present well compatibility. The addition of MAP-POSS reduces the T_p of PVC/CPE binary blend from 76°C to about 70°C. Moreover, the addition of MAP-POSS also broadens the mechanical loss tan δ peak. The mechanical loss tan δ peak range of C10M0 is from 50 to 95°C, and the mechanical loss tan δ peak range of PVC/CPE/MAP-POSS ternary system is from 40 to 100°C. This result is similar to the research of PVC/MAP-POSS blend by Soong et al.^{12,25} In general, an increase in the hard filler content leads to an increase in the storage modulus and a decrease in the maximum value of tan δ , but the position of the tan δ peak is generally constant.²⁶ The tan δ is a ratio of loss modulus E''and storage modulus E'. The lower tan δ value, the less energy dissipated. The maximum value of tan δ for C10M0 is 1.16, and the maximum value of tan δ for C10M3, C10M5, C10M7, and C10M10 is 1.08, 0.98, 0.97, and 0.93, respectively. Furthermore, T_p of C10M0 is 76°C, but almost every T_p of samples containing MAP-POSS is 70°C. These results are similar to the report of Wu et al.²⁶

Figure 8 shows the relationship between storage modulus E' and temperature *T*. PVC/CPE/MAP–POSS nanocomposites show a three-step storage modulus region. The first transition is about at -17° C, which is mainly associated with the glass transition of CPE phase, while the second transition at about 52°C (for PVC/CPE/MAP–POSS) or 64°C (for C10M0) mainly corresponds to the glass transition of PVC, E' in the last plateau, which is denoted as the rubbery modulus.

In general, an increase in the hard filler content leads to an increase in the storage modulus. In this work, the MAP–POSS as the filler added into PVC/CPE blends are equivalent to nanometer particles and have eight flexible methylacryloylpropyl groups on the outer of core. When a small amount of MAP–POSS is added into the systems, it will fill into free volume



Figure 7. Relationship between tan δ and temperature *T*. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 8. Relationship between storage modulus E' and temperature T. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between PVC and CPE molecule chains and decrease the η^* of melts. But, on the other hand, as previously described, the oxygen atom of methylacryloylpropyl on POSS can form weak hydrogen bond with PVC/CPE molecule. Furthermore, partial of MAP-POSS molecules or group can also cross-link with PVC or CPE molecule in the thermal process. That is, the polymer molecular chains will be adsorbed on MAP-POSS, and the "network structure" will be formed. These cross points will be a hindrance for the movements of PVC and CPE chains and increase the friction force between PVC, CPE chains, and MAP-POSS. Thus, the storage modulus increased when MAP-POSS is added. But the MAP-POSS also has a lubricant effect for molecular movement, when more MAP-POSS was added, a part of MAP-POSS will not be adsorbed or reaction with PVC/CPE chains, which will play a role of plasticizer. So, the storage modulus will decrease with increasing MAP-POSS content. Moreover, when MAP-POSS is added into systems, the glass



Figure 9. Relationship between loss modulus E'' and temperature *T*. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transition of PVC will occur at lower temperature. It also proves that MAP–POSS has a plasticizing effect to PVC/CPE blends.

Figure 9 shows the relationship between loss modulus E'' and temperature *T*. As seen from Figure 9, there are two peaks for each curve. The peak at about -23° C is mainly associated with CPE phase, and the other peak at about 55 and 67°C is mainly associated with PVC/CPE/MAP–POSS and C10M0 phase, respectively. The increasing MAP–POSS content leads to a decrease in both the two loss modulus peaks. The position of the loss modulus peak of CPE phase was only slightly changed, but the loss modulus peak temperature T_p of PVC phase was reduced from 67°C to about 55°C. And the addition of MAP–POSS also broadens the loss modulus peak range of PVC phase.

CONCLUSIONS

The MAP–POSS has an action of plasticizing to PVC/CPE blends, and it can decrease both the balance torque and plastic time during the processing. Both dynamic storage modulus G' and loss modulus G' of melts increase with increasing MAP–POSS content. Stress relaxation result of melts shows that elasticity of PVC/CPE melts increases with increasing MAP–POSS content.

The impact strength of PVC/CPE/MAP–POSS nanocomposites increases with increasing MAP–POSS content. When MAP–POSS content is 10 wt %, the blend has the best impact strength, and it is 5.38 kJ/m² higher than that of the PVC/CPE blend. Dynamic mechanical analysis result shows that the PVC/CPE blend is further plasticized with increasing MAP–POSS content, and the maximum value of tan δ decreased when MAP–POSS is added. The results showed that the MAP–POSS can be used as an efficient processing aid and impact modifier of PVC/CPE blend at appropriate content.

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