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Polyhedral oligomeric silsesquioxane as a novel plasticizer for poly(vinyl chloride)

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Abstract

This study focuses on investigating the use of polyhedral oligomeric silsesquioxanes (POSS) to plasticize poly(vinyl chloride) (PVC). Conventional organic plasticizers for PVC, such as dioctyl phthalate (DOP), are somewhat volatile, leading to plasticizer loss and unwanted deterioration of the material properties over time. Previous experimental results indicate that methacryl-POSS, which is much less volatile due to its hybrid organic–inorganic structure, has the ability to plasticize PVC. Methacryl-POSS is miscible in the PVC only up to 15 wt%, thereby limiting its suitability as a plasticizer. However, through the use of ternary compositions it is possible to increase the proportion of methacryl-POSS in PVC substantially. The T_g of appropriately formulated ternary PVC/POSS/DOP compounds can be reduced to near room temperature, and these materials exhibit desirable ductile behavior. Binary (PVC/DOP) and ternary (PVC/POSS/DOP) compounds formulated to the same T_g values showed considerably different mechanical properties. Such findings reveal the possibility of using POSS to engineer the mechanical properties of plasticized PVC.

Keywords: Polyhedral oligomeric silsesquioxanes (POSS); Poly(vinyl chloride) (PVC); Plasticizer

1. Background

Poly(vinyl chloride) (PVC) is the third most consumed polymeric material worldwide, with wide applications in areas including construction, tubing, medical devices and electronics packaging [1]. Due to the brittle nature of the neat PVC, it is often compounded with plasticizers to enhance its flexibility and toughness for various applications, and the most commonly used plasticizers for PVC are phthalate esters. Since dioctyl phthalate (DOP) was introduced in the 1930s, it has been the most widely used plasticizer. However, it is known that conventional low molecular weight organic plasticizers for PVC, such as DOP, are somewhat volatile, leading to plasticizer loss and unwanted deterioration of the material properties over the course of time. Furthermore, phthalate esters recently have been scrutinized for environmental and health related problems due to the leaching of plasticizer from the PVC matrix [2,3]. Many studies have been conducted to reduce the leaching and migration of plasticizers from the PVC materials [1]. Several alternative plasticizers and polymeric (oligomeric) plasticizers have been suggested to replace phthalate esters used in PVC [1,4,5]; surface modification techniques, such as crosslinking or coating the PVC surface, have also been developed to prevent leaching and improve the mechanical properties of plasticized PVC [1,6].

In our previous work, we have investigated the rate-dependent mechanical behavior of polyhedral oligomeric silsesquioxanes (POSS)-incorporated and DOP-plasticized PVC [7]. POSS has a hybrid organic–inorganic structure, which consists of a silica cage in the center with functional groups attached at the cage corners. The experimental results showed that the methacryl-POSS is miscible with PVC up to 15 wt%, and it reduces the glass transition temperature (T_g), yield

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stress, and modulus of the PVC. Furthermore, unlike DOP and most of the other commonly employed small molecule plasticizers, it does not result in antiplasticization [8] when incorporated in the polymer. Due to the hybrid organic–inorganic structure, POSS is also more stable and less volatile compared to the low molecular weight plasticizers. Unfortunately, its limited miscibility precludes the use of methacryl-POSS alone as a satisfactory plasticizer for PVC. Although the PVC/methacryl-POSS blends exhibited an increase in compliance over that of the neat PVC, the blends still failed in a brittle manner in tension at an engineering strain of 2% [7]. In this study, we explored the possibility of using a combination of methacryl-POSS and DOP as the plasticizer for PVC. First, a small amount of DOP was premixed into the PVC, and methacryl-POSS is then added. As will be shown, the small amount of DOP enhances the miscibility of POSS in PVC, achieving a wide range of tailorable mechanical properties including tensile ductility.

2. Experiments

2.1. Materials

Custom-made poly(vinyl chloride) (PVC) by Scientific Polymer Products, Inc. (Ontario, NY) was used in this study with an approximate molecular weight of 90,000 g/mol (reported by the supplier). The methacryl-POSS (mPOSS) was obtained from Hybrid Plastics (Fountain Valley, CA) and the dioctyl phthalate (DOP) was obtained from Sigma–Aldrich. Methacryl-POSS is a non-crystallizable mixture of 8, 10, 12, and 14-corner POSS cages, with 10-corner cages having the highest weight fraction. Fig. 1 shows the chemical structure of a 10-corner methacryl-POSS cage. At room temperature, methacryl-POSS does not crystallize and appears in the form of a light brown heavy oil. The pure methacryl-POSS has a glass transition temperature of −55 °C [9].

Various PVC/mPOSS and PVC/DOP binary blends and PVC/mPOSS/DOP ternary blends were prepared through melt blending using a lab scale extruder (DACA Instruments). Table 1 in Section 3 lists the compositions of the materials prepared in this study. The PVC used in all blends contained a 3 wt% thermal stabilizer (Thermolite® 890S, Atofina) in order to minimize degradation.

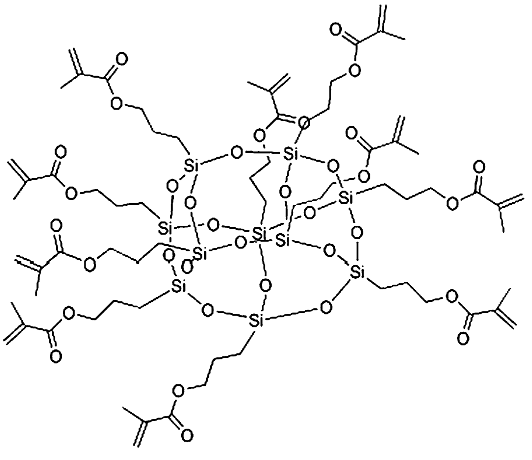

Fig. 1. Molecular structures of a 10-corner cage methacryl-POSS molecule.

2.2. Dynamic mechanical analysis

The thermomechanical behavior of the materials was characterized using TA instruments Q800 DMA over a temperature range from −120 °C to 120 °C with a 2 °C per minute heating rate at a frequency of 1 Hz. Cylindrical polymer samples with a diameter of 2.5 mm and a length of 15 mm were tested in the single cantilever mode in DMA with a fixed displacement of 25 μm. Storage modulus and loss modulus were measured as a function of temperature and the corresponding tan δ value was calculated by the TA Universal Analysis software.

2.3. Compression and tensile testing

The compression and tensile testing was performed on a Zwick mechanical tester (Zwick Roell Group). Extruded polymer strands were pelletized, compression molded into disks and then machined into specimens for compression testing. All specimens were machined to right circular cylinders with diameter of 9 mm and height of 4.5 mm. Thin Teflon films were placed between specimen and compression platens with WD-40 lubricant sprayed between the Teflon films and platens to reduce friction. A constant engineering strain rate of 0.001/s was applied to a final true compressive strain of −0.70. True strain is taken to be $\ln(h/h_0)$ with h being current sample height and h_0 being initial sample height; engineering strain is taken to be $\Delta h/h_0$.

Pelletized polymer blends were compression molded into dog-bone shaped specimens with gauge length of 25.4 mm, thickness of 1.6 mm, and width of 4.2 mm for tensile testing. Extensometers were employed in tensile testing to determine the tensile strains. All specimens were tested at a constant engineering strain rate of 0.001/s until failure occurred. Three specimens were tested for every blend to ensure the repeatability.

Table 1
α-Transition temperature (T_g) and FWHM of all PVC blends

	PVC (wt%)	mPOSS (wt%)	DOP (wt%)	T_g (°C)	FWHM (°C)
PVC	100	0	0	84.8	15
5DOP	95	0	5	76.9	18
10DOP	90	0	10	65.0	10
15DOP	85	0	15	56.2	57
20DOP	80	0	20	47.5	64
40DOP	60	0	40	5.6	40
5mPOSS	95	5	0	82.5	20
10mPOSS	90	10	0	77.3	22
15mPOSS	85	15	0	74.0	20
15mPOSS5DOP	80	15	5	66.1	40
20mPOSS5DOP	75	20	5	62.5	51
25mPOSS5DOP	70	25	5	59.3	65
20mPOSS20DOP	60	20	20	25.6	47

2.4. Accelerated test for plasticizer loss

The loss of volatile plasticizers from PVC compounds has been measured in various accelerated testing schemes [10–12]. Here, we have held the compounds for two weeks in a vacuum oven at 85 °C to monitor this phenomenon. All of the plasticized blends were first pelletized and tested in one batch in order to minimize the experimental error due to any vacuum or temperature variations in the oven. The sample weight was measured before and after the vacuum oven treatment, and the percent weight loss of each PVC blend was calculated.

3. Results and analysis

3.1. Dynamic mechanical analysis

3.1.1. PVC/mPOSS/5 wt% DOP

Previous research in our laboratories has shown that methacryl-POSS plasticizes PVC [7]. However, methacryl-POSS was found to be miscible in the PVC only up to 15 wt% with a reduction in α-transition temperature (also known as the T_g) of 10.8 °C. With POSS concentration above 15 wt%, the material became opaque and sub-micron sized POSS aggregates were observed in the transmission electron microscopy images [7].

Ternary blends containing 5 wt% DOP in PVC with addition of 15 wt%, 20 wt% and 25 wt% methacryl-POSS were prepared for this study. The addition of 5 wt% DOP increases the amount of POSS that can be incorporated into the compound in a miscible manner up to 25 wt% and all blends appear to be transparent and homogeneous. Fig. 2 shows the storage modulus, loss modulus, and tan δ curves for the PVC/5 wt% DOP and the ternary PVC/mPOSS/5 wt% DOP blends. With increasing methacryl-POSS content, the PVC is further plasticized. The addition of 25 wt% methacryl-POSS reduces the α-transition temperature of the PVC/5 wt% DOP from 77 °C to 59 °C based on the tan δ peak value at 1 Hz. The addition of POSS also broadens the α-peak; the 25 wt% addition of the POSS increases the FWHM[1] of the loss modulus α-peak from 18 °C to 65 °C. Although the α-transition temperature of the 70 wt% PVC/25 wt% mPOSS/5 wt% DOP blend is 59 °C based on the tan δ peak value, the α-transition occurs over a broad temperature range from −40 °C to 60 °C (Fig. 2). Therefore, the material is in the leathery regime at room temperature with a storage modulus value around 1000 MPa.

Less distinguishable β-transition peaks and wider α-peak shoulders on the lower temperature side were also observed in both the loss modulus and the tan δ curves with increasing POSS concentration. The observation of the shoulder results from the merging of the β-transition peak into the α-peak when the material is more plasticized and exhibits a lower α-transition temperature.

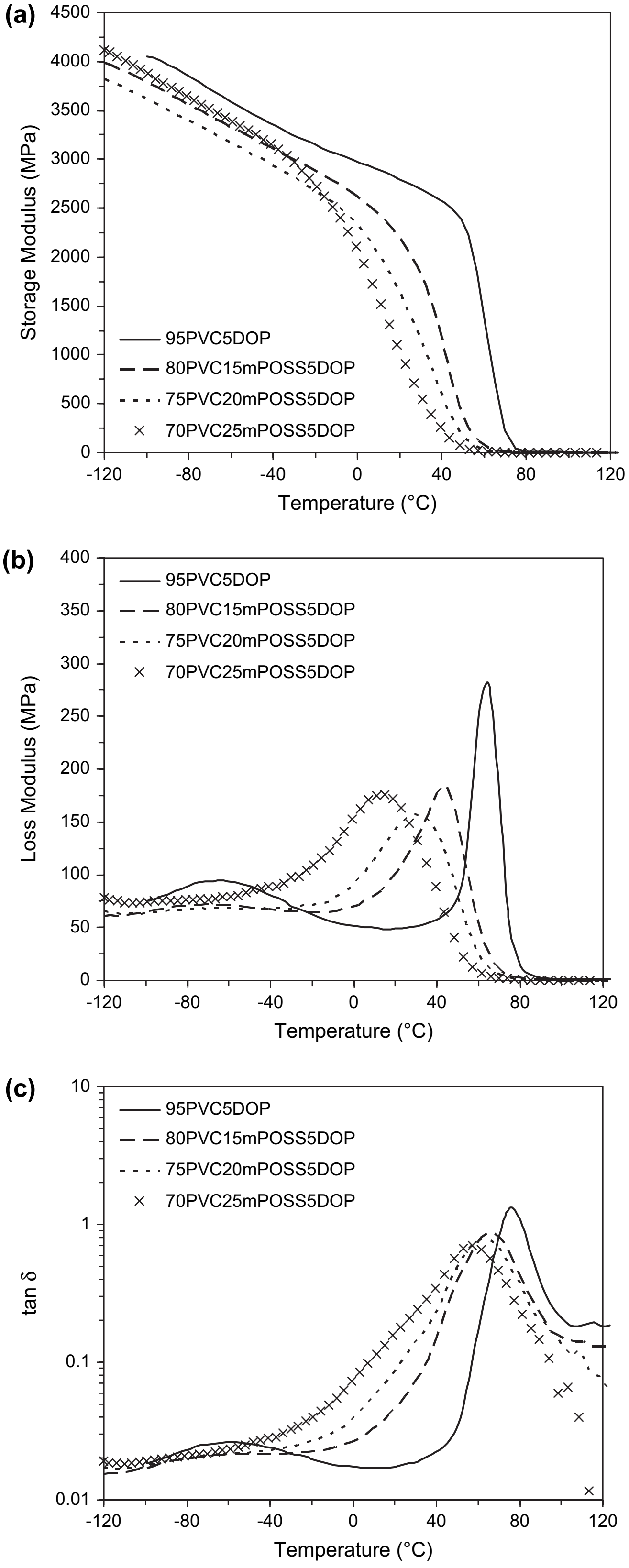

Fig. 2. Storage modulus (a), loss modulus (b), and tan δ (c) curves of PVC/mPOSS/5 wt% DOP blends as a function of temperature at 1 Hz.

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[1] FWHM (full width at half maximum) here is defined as the breadth (duration of temperature) of the transition peak at half of its maximum peak value.

3.1.2. 60 wt% PVC/mPOSS/DOP

Two heavily plasticized PVC blends (60 wt% PVC/40 wt% DOP and 60 wt% PVC/20 wt% mPOSS/20 wt% DOP) were prepared and characterized. Fig. 3 shows the storage modulus, loss modulus, and tan δ curves of the two materials as a function of temperature at 1 Hz. The peak values of the tan δ curves indicate that the α-transition temperatures of the 60 wt% PVC/40 wt% DOP and the 60 wt% PVC/20 wt% mPOSS/20 wt% DOP are 5.6 °C and 25.6 °C, respectively. The onset of the broad α-transition of both compounds occurs at a much lower temperature, near −60 °C.

3.1.3. DOP vs. mPOSS as plasticizers

Table 1 summarizes the compositions, the α-transition temperatures (T_gs),[2] and the FWHM[3] of all the PVC blends prepared. Incorporating DOP and/or methacryl-POSS reduces T_g, and DOP appears to be a more effective plasticizer than methacryl-POSS when compared on the basis of weight fraction of the plasticizer in the compound (Fig. 4a). If the effect of the methacryl-POSS or DOP is evaluated on a basis of moles of plasticizer in the compound (Fig. 4b), both plasticizers have essentially the same influence on T_g. Furthermore, the T_gs of the ternary blends show a linear combination of the plasticizing influence of the two molecules when considered on the basis of the molar amount of plasticizer per gram of compound. Fig. 4b shows the linear regression curve that was constructed from the T_gs of various PVC blends, and it can be used to anticipate the T_g of all other homogeneous binary and ternary blends that can be produced with this system of components.

3.2. Mechanical testing

3.2.1. PVC/mPOSS/5 wt% DOP

Fig. 5 shows the uniaxial compression true stress–true strain curves of the ternary blends containing 5 wt% DOP at a strain rate of 0.001/s. With the increasing amount of methacryl-POSS in PVC, the compounds become more plasticized. The materials transition from glassy to leathery behavior with significant reductions in the yield stress and the flow stress.

Fig. 6 shows the uniaxial tension true stress–true strain curves of the PVC ternary blends at 0.001/s strain rate. The PVC/5 wt% DOP blend exhibits brittle behavior in tensile testing, where all specimens failed at a strain less than 5%. Incorporating 15 wt% methacryl-POSS in PVC containing 5 wt% DOP changed the tensile behavior from brittle to ductile and the strain at break was improved to approximately 70% in true strain (nearly 100% in engineering strain).

3.2.2. 60 wt% PVC/mPOSS/DOP

Figs. 7 and 8 present the true stress–true strain curves of 60 wt% PVC/40 wt% DOP and 60 wt% PVC/20 wt%

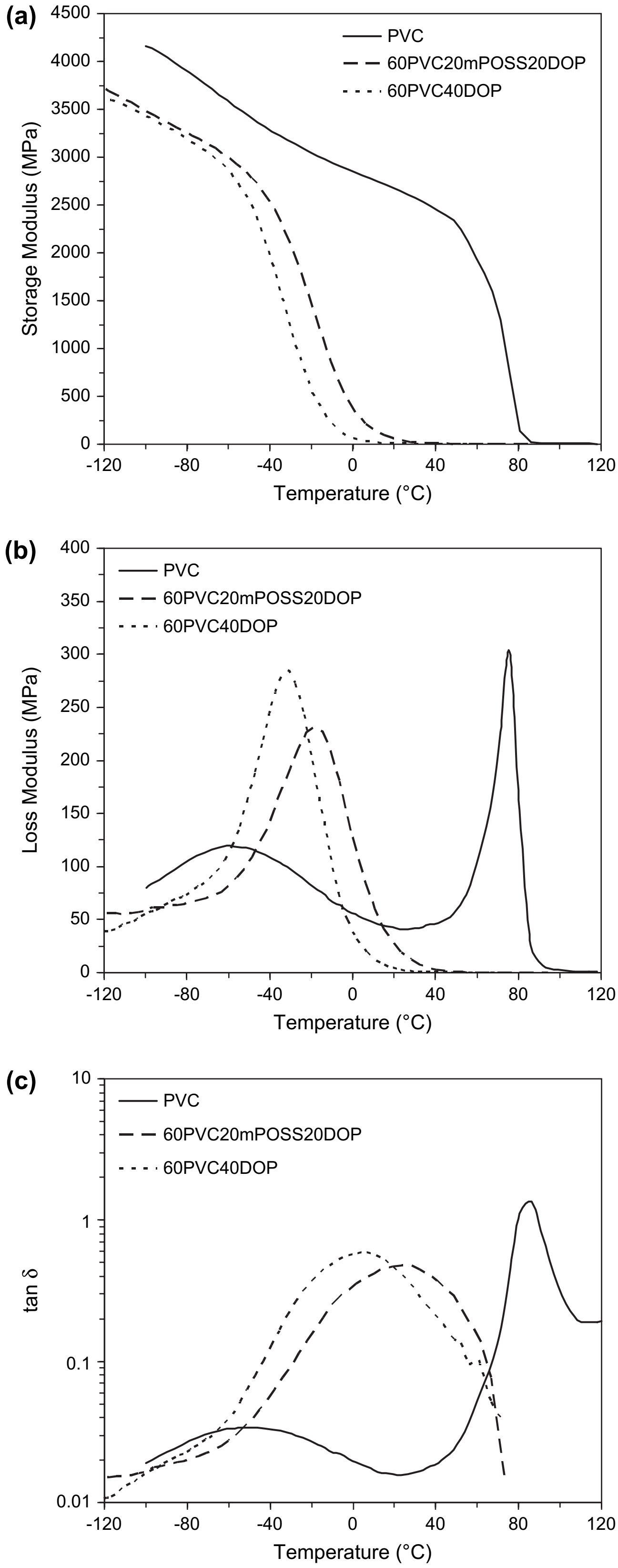

Fig. 3. Storage modulus (a), loss modulus (b), and tan δ (c) curves of PVC/mPOSS/DOP blends as a function of temperature at 1 Hz.

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[2] α-Transition temperature is based on the tan δ peak value at 1 Hz measured in DMA.

[3] FWHM is defined as the FWHM of the loss modulus transition peak at 1 Hz in DMA.

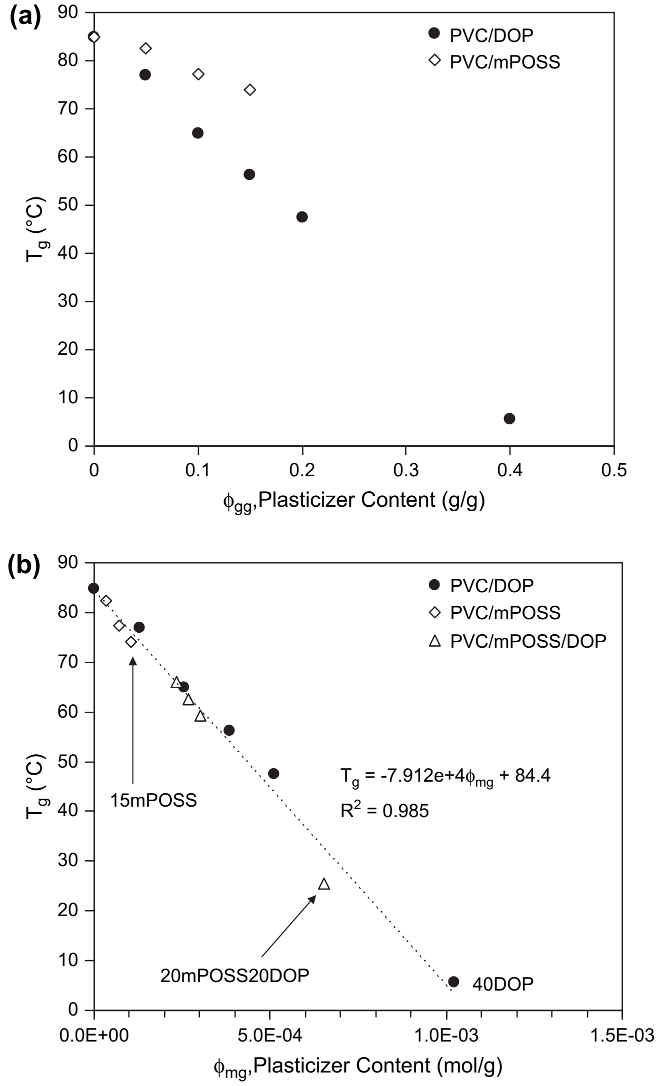

Fig. 4. T_g as a function of the plasticizer content: on a basis of grams of plasticizer per gram of compound (g/g) (a) and moles of plasticizer per gram of compound (mol/g) (b).

mPOSS/20 wt% DOP in uniaxial compression and tension, respectively, each at a strain rate of 0.001/s. Both PVC compounds are heavily plasticized and exhibit rubbery behavior.

3.3. Stability of the plasticized compounds

The stability of the plasticized compounds was evaluated by determining the percent weight loss of the sample pellets after being held in a vacuum oven at the 85 °C/two-week oven test. Fig. 9 shows the percent weight loss of samples containing various loadings of methacryl-POSS or DOP in PVC as a function of the weight percent of the plasticizer. The weight loss is negligible in all of the PVC/methacryl-POSS blends. A 5% weight loss was observed in the PVC/20 wt% DOP blend and a 25% weight loss was observed in the PVC/40 wt% DOP blend. Assuming all the weight loss is attributed to the loss of DOP, more than 20% of the original DOP added in the PVC/20 wt% DOP blend and more than 50% of the initial amount of DOP in the PVC/40 wt% DOP blend was lost over the duration of our accelerated test.

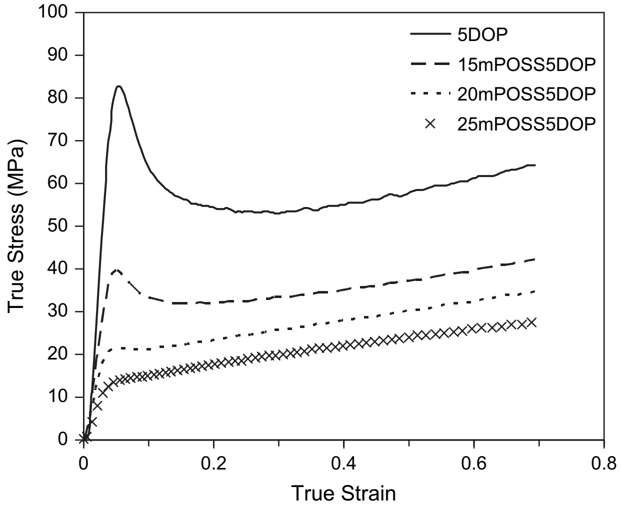

Fig. 5. True stress–true strain curves of compounds containing 5 wt% DOP and various amounts of methacryl-POSS. Testing was done in uniaxial compression at 0.001/s.

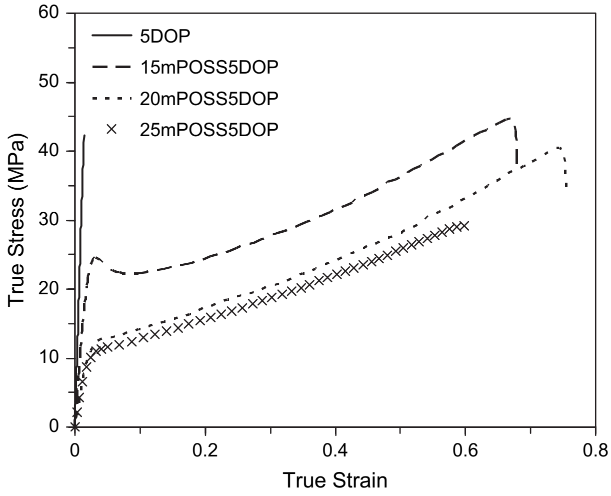

Fig. 6. True stress–true strain curves of compounds containing 5 wt% DOP and various amounts of methacryl-POSS. Tensile testing conducted at 0.001/s.

To compare the stability of methacryl-POSS and DOP on the basis of its effectiveness as a plasticizer, Fig. 10 shows the percent weight loss as a function of the original reduction in T_g afforded by the added plasticizer. Due to the limited solubility of methacryl-POSS in PVC, the performance of PVC/methacryl-POSS blends is indistinguishable from that of the PVC/DOP blends in the limited range of overlap of the data.

In order to evaluate the stability of the ternary blends compared to the PVC/DOP compounds, we considered the resulting increase in T_g that arises due to plasticizer loss; we denote this parameter as "T_g penalty" in Fig. 11. Because of the observed molar character of the plasticization phenomenon, this parameter is a better measure of compound stability than weight loss. Since methacryl-POSS shows essentially no volatility in all of our oven tests, we assume that all the weight loss in any ternary blend can be attributed to the DOP. The

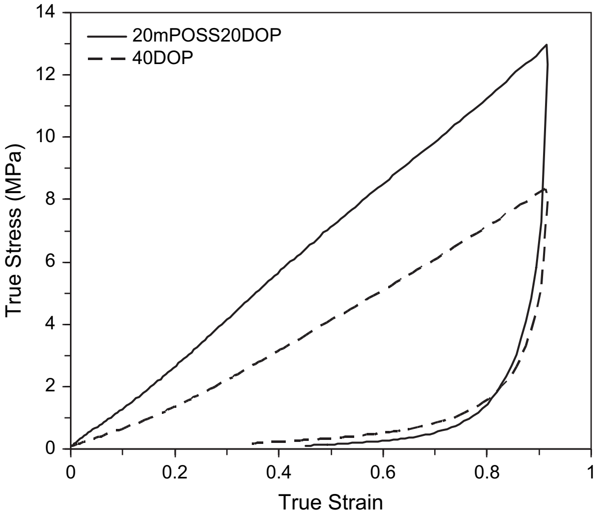

Fig. 7. Uniaxial compression true stress–true strain curves of compounds containing 40 wt% plasticizer, at a nominal strain rate of 0.001/s.

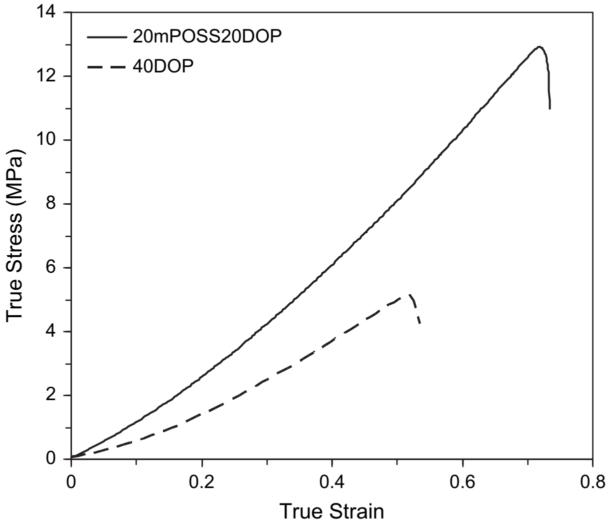

Fig. 8. Uniaxial tension true stress–true strain curves of compounds containing 40 wt% plasticizer, at a nominal strain rate of 0.001/s.

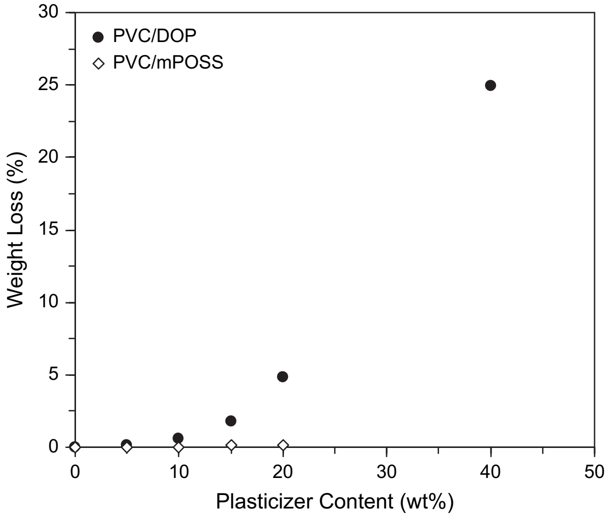

Fig. 9. The percent weight loss of the PVC/mPOSS and the PVC/DOP blends as a function of the plasticizer content (wt%).

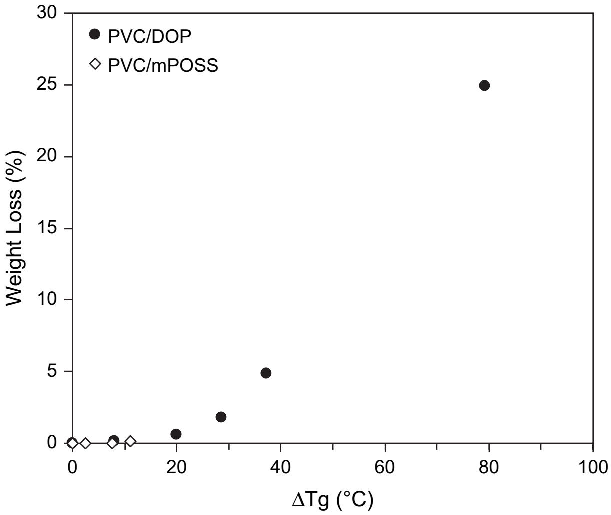

Fig. 10. The percent weight loss of the PVC/mPOSS and the PVC/DOP blends as a function of the original reduction in T_g.

expected regain in T_g (T_g penalty) was then calculated based on the loss of DOP using the linear regression equation (Fig. 4b). Fig. 11 shows that the T_g penalty for the PVC/DOP blends, PVC/methacryl-POSS blends and PVC/methacryl-POSS/DOP blends all collapse into a single curve. Therefore, as in the case of T_g reduction, the stability of the various ternary compounds over the time frame of our accelerated test can be predicted from measurements on the two binary compounds. There is no synergistic effect of the methacryl-POSS on retention of DOP in the compounds tested. In all cases we expect that the formulated amount of methacryl-POSS would remain in the PVC indefinitely.

4. Discussion

In this section we will discuss the potential of using methacryl-POSS and/or DOP as a plasticizer for PVC to engineer the mechanical properties of plasticized PVC blends possessing the same T_g.

4.1. Antiplasticization: DOP vs. mPOSS

Fig. 12a shows the true stress–true strain curves of PVC/DOP blends in compression testing at a nominal strain rate of 0.001/s. The yield stress of the 5 wt% DOP blend exceeded the yield stress of the neat PVC; such behavior is known as antiplasticization and has been well documented in PVC materials containing relatively low concentrations of plasticizer [8,13–15]. In the case of the 5 wt% DOP compound, antiplasticization is due to the strong affiliation between the aromatic rings of the plasticizer and the PVC backbones, which hinders the local short segmental motions (β-motions) [13,16]. The restricted β-motions in the 5 wt% DOP blend impose an additional resistance at the point of yield, resulting in a higher

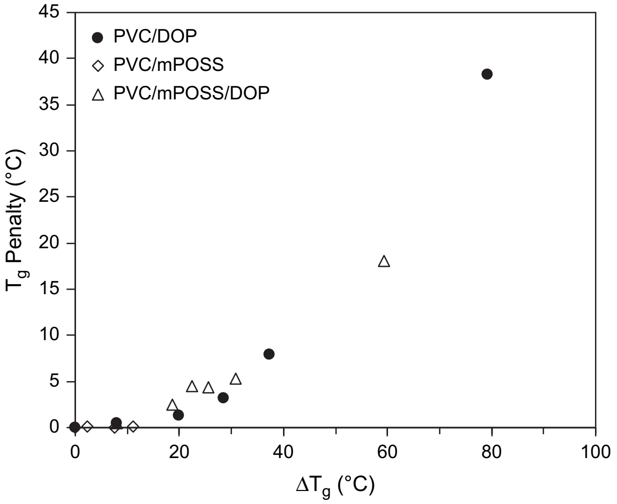

Fig. 11. T_g penalty (calculated) due to the loss of DOP as a function of the original reduction in T_g.

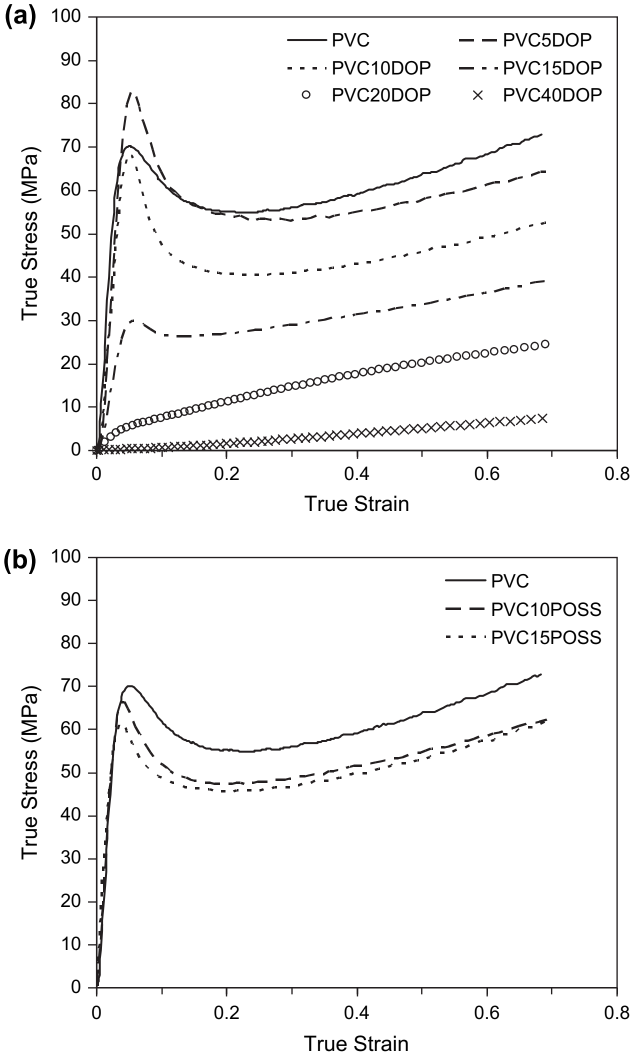

Fig. 12. True stress–true strain curves of the PVC/DOP (a) and the PVC/mPOSS (b) in compression testing at 0.001/s.

yield stress compared to neat PVC. However, a dramatic post-yield strain softening is observed in the 5 wt% DOP compound and its post-yield strain-softened flow stress falls beneath that of the neat PVC. During steady plastic flow in a glassy polymer, the molecular mobility is locally enhanced to a level equal to that of the rubbery state [17]. Here we see that this effect also acts to locally liberate the antiplasticized β-motions in PVC as evidenced by the post-yield flow stress of the 5 wt% DOP blend falling beneath the neat PVC flow stress.

The significant antiplasticization effect seen in the PVC/DOP compounds was not observed in the PVC/mPOSS blends, as shown in Fig. 12b where the initial yield stress of the PVC/POSS blends is always lower than that of the neat PVC. This observation is consistent with our earlier studies of this system, and differences in molecular size and shape of methacryl-POSS and DOP account for this behavior [7].

4.2. Same T_g, different mechanical properties

Fig. 13a shows the storage modulus and tan δ curves of the PVC/5 wt% DOP and PVC/10 wt% mPOSS blends. The two

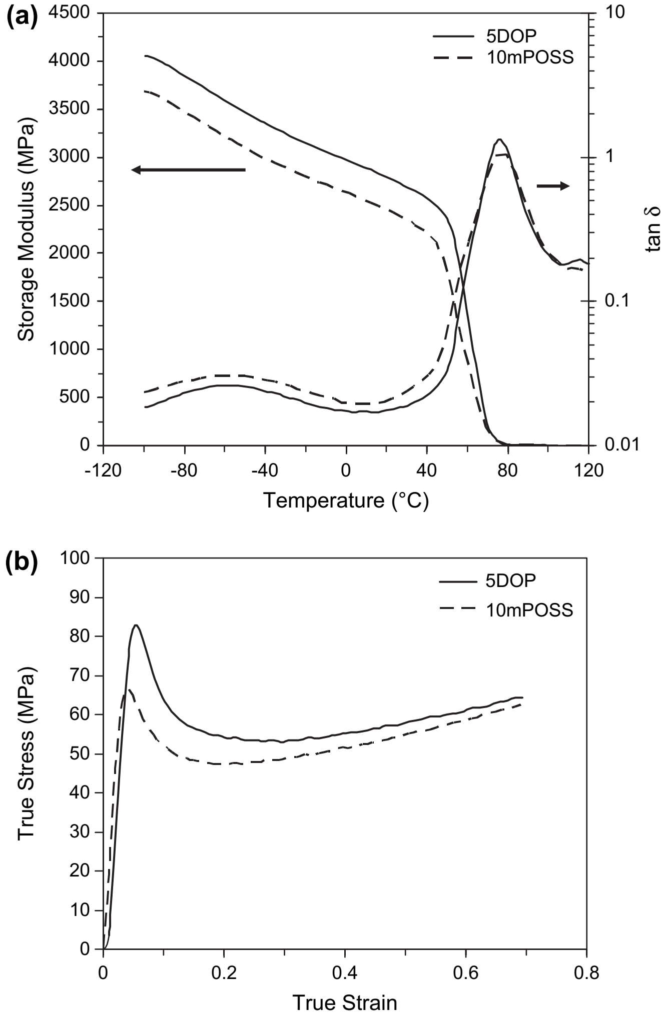

Fig. 13. Storage modulus and tan δ curves (a) and true stress–true strain curves in compression testing (b) of 95 wt% PVC/5 wt% DOP and 90 wt% PVC/10 wt% mPOSS.

blends have nearly identical T_g based on the tan δ peak value; however, their room temperature mechanical properties are quite different. Due to the antiplasticization effect, the room temperature storage modulus (Fig. 13a) of the 5 wt% DOP is greater than that of the 10 wt%/methacryl-POSS; additionally, the initial yield stress of the 5 wt% DOP compound is much higher than the value exhibited by 10 wt% methacryl-POSS blend in the compression testing (Fig. 13b) since the 5 wt% DOP blend has the extra barrier to yield due to the hindered β-motions. Interestingly, the post-yield strain-softened behavior of the two materials is nearly identical since the initially hindered β-motions of the PVC/5 wt% DOP material are locally liberated during active flow.

In a second example, we used the regression equation from Fig. 4b to prepare a ternary blend that has the same T_g (56.2 °C) as the PVC/15 wt% DOP compound. We fixed the ternary compound to contain 10 wt% DOP and then back-calculated the amount of methacryl-POSS and PVC required to achieve the target T_g. The regression equation predicted that 17.5 wt% methacryl-POSS with 10 wt% DOP in PVC should exhibit the same T_g as the PVC/15 wt% DOP blend. Fig. 14a shows the tan δ curves of the two blends. The two tan δ peak values are approximately equivalent, which confirms the prediction made by the regression equation.

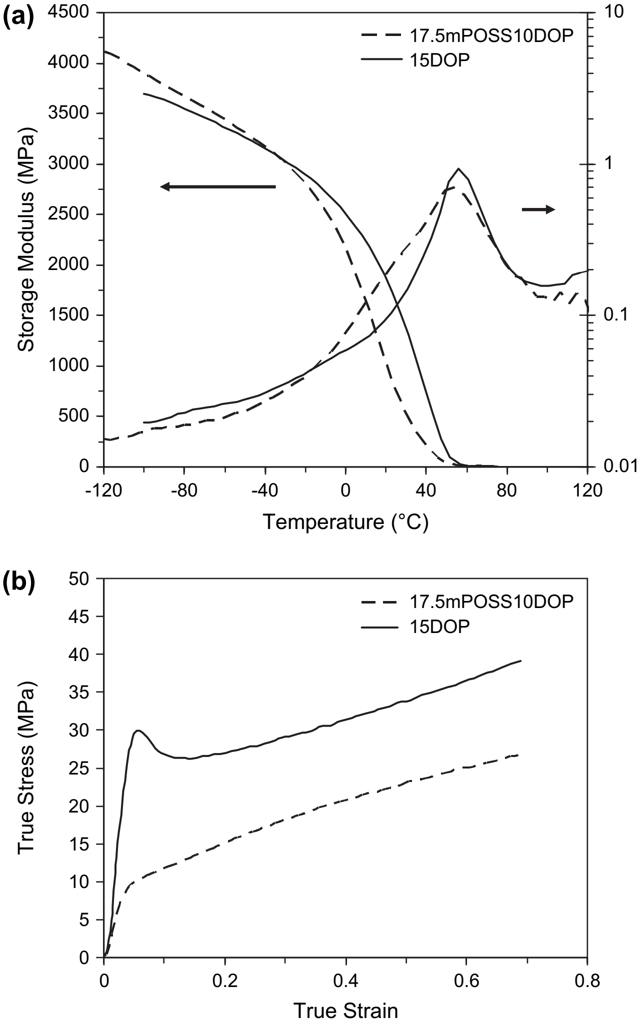

Fig. 14. Storage modulus and tan δ curves (a) and true stress–true strain curves in compression testing (b) of 85 wt% PVC/15 wt% DOP and 72.5 wt% PVC/17.5 wt% mPOSS/10 wt% DOP.

Fig. 14b presents the true stress–true strain curves of the two blends in compression testing. Although the T_gs of the two blends are nearly identical, their true stress–true strain curves are significantly different. While the PVC/15 wt% DOP compound still shows a near glassy polymer behavior, the ternary blend is leathery/nearly rubbery at room temperature in low rate compression testing. The distinction in mechanical behavior between the two blends is attributed to the different molecular level modifications offered by DOP and methacryl-POSS. Fig. 14a suggests that the methacryl-POSS in the ternary blend created a broader transition and shoulder on the lower temperature side of the α-peak, and the onset of α-transition appears at a lower temperature compared to the DOP-plasticized PVC. Fig. 14a also shows that the storage modulus of the ternary blend is significantly lower than the 15 wt% DOP compound when crossing the room temperature regime due to the breadth of the α-transition.

Fig. 14 demonstrates clearly the possibility to engineer a series of methacryl-POSS and DOP-plasticized PVC compounds that possess the same T_g but exhibit significantly different mechanical properties.

5. Conclusions

Previous research demonstrated that methacryl-POSS plasticizes PVC without causing antiplasticization, which is frequently observed when small organic plasticizers are used. However, using methacryl-POSS to plasticize PVC to room-temperature-flexible compounds was not possible due to the miscibility limit [7]. In this study we demonstrate that the addition of a small amount of DOP increases the miscibility of methacryl-POSS in PVC substantially. With 5 wt% DOP added in the polymer blend, the amount of methacryl-POSS that can be incorporated into the compound was increased from 15 wt% to 25 wt%. The T_gs of the ternary PVC compounds can be reduced to near room temperature, and the material becomes leathery to nearly rubbery and exhibits ductile tensile behavior.

Comparing methacryl-POSS and DOP on a basis of moles of plasticizer added per gram of compound reveals that the two additives are equally effective in reducing the T_g of PVC. The T_gs of methacryl-POSS, DOP, and POSS/DOP-plasticized PVC blends formed a linear relationship when plotted on this basis. The regression line can be used to anticipate the T_g of other homogeneous binary and ternary blends. The POSS/DOP-plasticized PVC did not show any synergistic effects in retaining the plasticizer in the PVC compounds through the duration of the oven tests conducted. However, the POSS/DOP-plasticized PVC demonstrated considerably different mechanical behavior in low rate compression and tensile experiments when compared to the DOP-plasticized PVC which has the same T_g. Such findings reveal the possibility of using POSS to engineer the material properties of plasticized PVC compounds.

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