POSS Reinforced PVC Nanocomposites

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Abstract Over the past few years, research into polymers containing polyhedral oligomeric silsesquioxane (POSS) has grown, emphasizing new categories of polymer/polyhedral oligomeric silsesquioxane nanocomposite materials as well as previously unidentified uses. Due to the nano-scale size of polyhedral oligomeric silsesquioxane, these hybrids provide exceptional structural and functional qualities (strength, thermal stability, optical characteristics, low toxicity, and biocompatibility). This book chapter reviews the current development of polyhedral oligomeric silsesquioxane-reinforced poly(vinyl chloride) (PVC) systems. Chlorine atoms in PVC make it a more rigid and stiffer material by increasing the intermolecular attraction between polymer chains. These hybrid POSS nanofillers were found to be simple to incorporate into PVC and may be able to construct, reinforce, and stabilize materials more effectively than conventional ones. The key focus of this chapter was the morphological, thermal, mechanical, and rheological properties of the POSS reinforced PVC nanocomposites.

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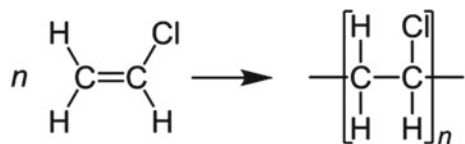
1 Introduction

Poly(vinyl chloride) (PVC) is a commodity synthetic polymer produced in second large amounts after polyethylene (PE). PVC is a thermoplastic polymer and is one of the three (PE, polypropylene (PP), and PVC) most important polymers currently used in the worldwide. PVC is one of the most economical polymers to make and has an extensive range of properties so that it can be used for hundreds of applications. PVC is polar in nature, and it is resistant to nonpolar solvents. Also, it is a flame-retardant and self-extinguishing polymer. Pure PVC is a white, brittle solid (although different PVC variants are designed to be very flexible) and strong. PVC is obtained by polymerizing vinyl chloride (chloromethane) monomer units, as can be seen in Fig. 1 [1–3].

Vinyl chloride is a colorless, combustible, and narcotic gas created by synthesizing ethylene and chlorine from petroleum thermal cracking and membrane electrolysis of rock salt. The membrane process produces caustic soda and hydrogen, used as raw ingredients in various processes. In different polymerization procedures, stabilizers and plasticizers are added to the monomer vinyl chloride to produce PVC (radical or ionic).

Synthetic resin is made by reacting vinyl chloride and other monomers in agitated pressure vessels in the presence of catalysts and then converting the liquids and/ or gases to solid resin. The reaction produces a significant amount of heat, and the vessel is cooled to remove this. The rate of reaction slows as the monomer is converted to polymer; hence, after an optimum reaction period, the unconverted residual monomer is removed from the reacting mass by heat and vacuum, and the resin (PVC) is recovered as a dry white powder, liquid latex, or solution. This polymerization reaction can occur in a pure monomer, a solution, a water-monomer emulsion, or a monomer water suspension. The type of polymerization process determines the type of recovery method and resin particles produced [4]. Vinyl chloride (VC) is produced via four processes; bulk polymerization process [5], suspension polymerization process [6], emulsion polymerization process [7], and solution polymerization process [8]. Suspension polymerization and emulsion polymerization have been the most widely used processes for many years. Suspension polymerization (Fig. 2) is the most common method for producing PVC resins, accounting for 82–85% of output produced in the United States. It comprises charging an agitated reactor with one or two parts water and one-part vinyl chloride monomer or comonomer combination, as well as initiator and suspending agents such poly(vinyl alcohol).

The mass is reacted at 50–65 °C until around 85–90% of the monomer is transformed into the resin. The unconverted monomer is removed from the resin water

Fig. 1 Polymerization of vinyl chloride
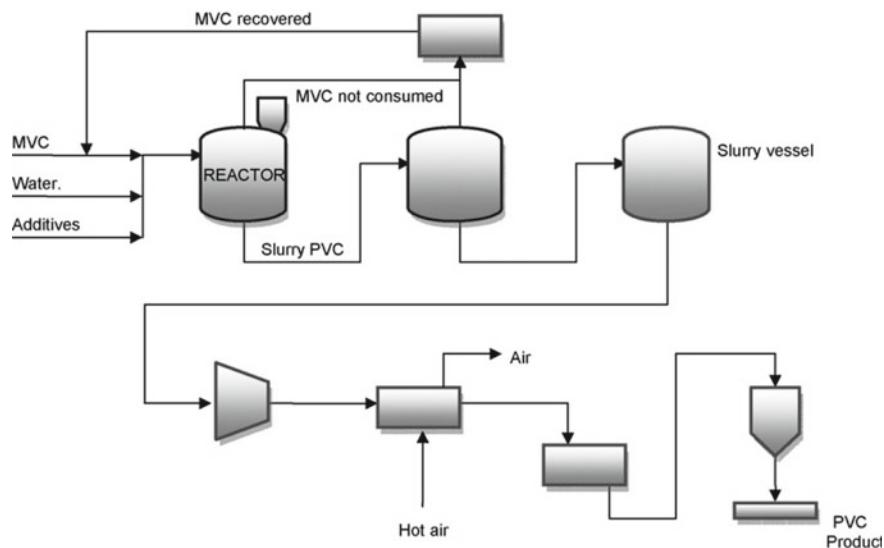
Fig. 2 Simplified flowsheet of the PVC production process by suspension [9]

mixture by heating it, often under a vacuum. The resin is subsequently taken from the water and dried by exposure to warm air in rotary, flash, or fluid bed driers before being delivered to storage silos. The high productivity per unit reactor volume, flexibility in polymer composition and resin particle properties, and granular nature of the product are all advantages of the suspension resin process. The problem with this process is the larger resin particle size (50–150 μm), making it challenging to remove unconverted vinyl chloride monomer [4, 9, 10].

Emulsion polymerization is the second most common method for producing PVC resins, accounting for 10–12% of total output in the United States. One of the most critical parts of emulsion polymerization is that it is a diverse range of processes that each produce specialized products that are defined or specified in terms of performance in a particular application. In addition to the reactor fouling issue described for suspension polymerization, the emulsion polymerization process provides less flexibility in terms of changing process variables. Furthermore, emulsion process resins are costly to produce, and plant operators are more conservative regarding process modifications. Also, more vinyl chloride monomer is emitted in this process, which affects workers' health as well. Bulk and solution polymerization account for 5–7% of total PVC output in the United States [4, 11–13].

The presence of a chlorine atom increases intermolecular attractions between polymer chains, making PVC a more rigid and stiffer material. Window frames, drainage pipe, water service pipe, medical devices, blood storage bags, cable and wire insulation, resilient flooring, roofing membranes, stationary, automotive interiors and seat coverings, fashion and footwear, packaging, cling film, credit cards,

vinyl records, synthetic leather, and other coated fabrics are just some of the applications for PVC [1, 2, 14–20]. PVC that has not been compounded is colorless and hard, with poor heat and light stability. However, by using additives/stabilizers, we can adjust the qualities of PVC to our requirements and applications. In recent years, the blending of polymers has been deemed the most suitable approach for obtaining balanced and needed qualities in hybrid polymeric materials. Because these required features cannot be acquired from a single polymeric component, blending two or more polymers has emerged as a new technique for achieving innovative and desirable uncommon properties, such as mechanical, thermal, morphological, rheological, and chemical properties. Polymeric hybrids/composites are widely employed in a wide range of items, including footwear, medical equipment, automobiles, packaging, and space transportation [21–24]. Researchers have recently considered nanoparticles for incorporating into polymer blends because of their extraordinary physical and chemical properties, notably their nano size ranges of 10 nm to 1 μm. Their applications can be found in various industrial, commercial, and consumer products. Because of these applications, nanoparticles must be analyzed precisely and thoroughly based on their nanostructure.

To give maximum mechanical and thermal benefits, polyhedral oligomeric silsesquioxane (POSS), a nanostructured chemical, is used as a building block in polymer matrices of blends [13, 25]. In recent decades, polyhedral oligomeric silsesquioxanes (POSSs) have been employed as filler, nucleating agent, crosslinker, and adhesion promoter [26–32]. POSSs are a new generation of hybrid nanofillers that combine organic and inorganic nanoscale structures. These hybrid nanofillers (POSSs) are expected to be easy to incorporate into polymers, including PVC. They may be able to build, reinforce, and stabilize materials compared to traditional ones [29, 32–35]. POSS is a nanosized hybrid with a chemical composition that is intermediate between silica (SiO_2) and silicon (SiO_2) (R_2SiO). A silsesquioxane is an organosilicon compound having the chemical formula $[RSiO_{1.5}]_n$, where R is an organic functional group (aryl, alkyl, or alkoxyl) with reactive and/or non-reactive groups. Silsesquioxanes are colorless solids with Si–O-Si connections that form cages or polymeric structures. Silsesquioxanes have two types of molecular structures: caged and non-caged [22, 29, 36]. Figure 3 illustrates the chemical structures of various functionalized POSS types. Researchers are attracted to them because of their unique structure, which has an organic shell and an inorganic silicate core. The inorganic silicate core provides a significant improvement in thermal characteristics and stiffness of materials, among other things. Unlike silica, POSS molecules, made up of reactive functional groups linked covalently, are suitable for polymerization and integration into different polymer blend systems. Because the POSS technology is chemically versatile, several POSS monomer and polymer systems are being developed or have already been produced. POSSs come in various molecular structures, including 6, 8, 10, and 12 Si vertices denoted T_6, T_8, T_{10}, and T_{12} (T = tetrahedral vertex). POSS molecules with a T_8 cubic inorganic core composed of silicon-oxygen ($R_8Si_8O_{12}$) are the most often studied structures in POSS molecules [37–40].

Furthermore, the hybrid organic–inorganic framework makes POSS thermally and chemically robust. One of the most promising uses for POSS-based polymers
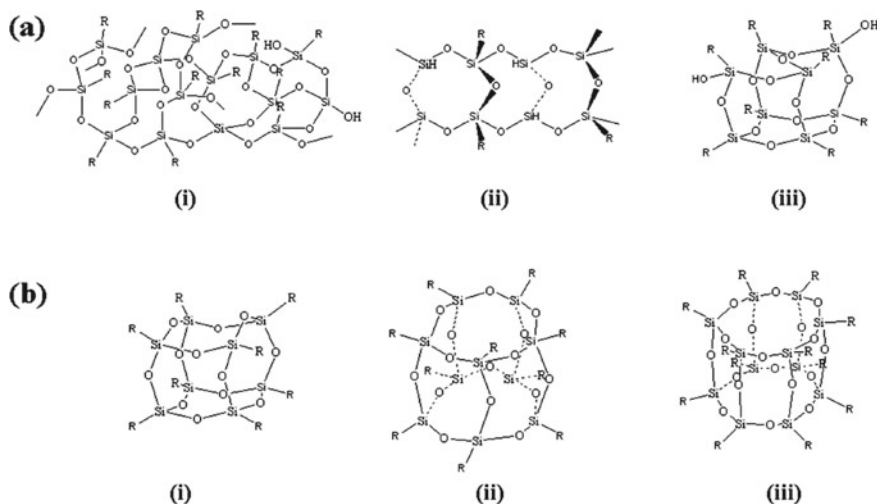
Fig. 3 Chemical structures of silsesquioxanes. **a** non-caged silsesquioxanes: (i) random, (ii) ladder; (iii) partial caged structures, and **b** caged silsesquioxanes: (i) T_8, (ii) T_{10}, (iii) T_{12} structures [40]

is in the highly oxidizing environment of orbiting spacecraft. POSS can improve polymers' oxidative stability and flame retardance in terrestrial applications, similar to the atomic oxygen resistance trend [41–43].

This chapter has comprehensively discussed the impact of POSS incorporation on the mechanical, thermal, rheological, and morphological properties of PVC and its nanocomposites.

2 Mechanical, Dynamic Mechanical, and Morphological Properties of POSS Reinforced PVC Nanocomposites

As a significant commercial polymer, PVC has been studied extensively in industrial applications for many years. PVC and its composites, on the other hand, are limited in several applications due to underlying deficiencies such as lower heat softening temperature and high brittleness (low toughness). Therefore, new PVC products with high quality must be developed to generate high added values and expand PVC applications. Some studies have been conducted to improve the mechanical properties of PVC using nanoscale reinforcement additives. The main goal is to use molecular or nanoscale reinforcements to enhance the strength and toughness of polymeric components [44–46]. This section presents the mechanical, dynamic-mechanical, and morphological findings from studies involving PVC matrix and several types of POSS nano additives.

In a study by Du et al., PVC/ octyl-POSS (O-POSS) composites containing O-POSS at 0, 1, 1.5, 2, 2.5, and 3 wt% were prepared using a two-roll laboratory mill.

Then, to observe the mechanical properties, 1 mm and 5 mm thickness nanocomposite plates were obtained by pressing these mixtures at 180 °C. The resultant composite samples were then subjected to various analyses such as tensile, impact strength, and dynamic mechanical analysis (DMA). Figure 4 shows that as the weight content of O-POSS in the PVC matrix increases, the tensile strength drops constantly. Moreover, according to the impact strength results, an increment in impact strength values was observed up to 1.5 wt% O-POSS content, while the impact strength value was decreased as the O-POSS contents were increased from 1.5 wt%. When O-POSS content exceeds 1.5 wt%, phase separation occurs, and impact strength drops. This is because adding O-POSS reduces the molecular frictional force or entanglement of PVC chains or particles, resulting in a reduction in tensile strength. This phase separation was proved via SEM images, as seen in Fig. 5.

As a result of the scanning electron microscopy (SEM) observations performed on the impact test samples, it was observed that the samples without O-POSS exhibited a brittle fracture behavior (Fig. 5 P1). In contrast, the samples containing 1%
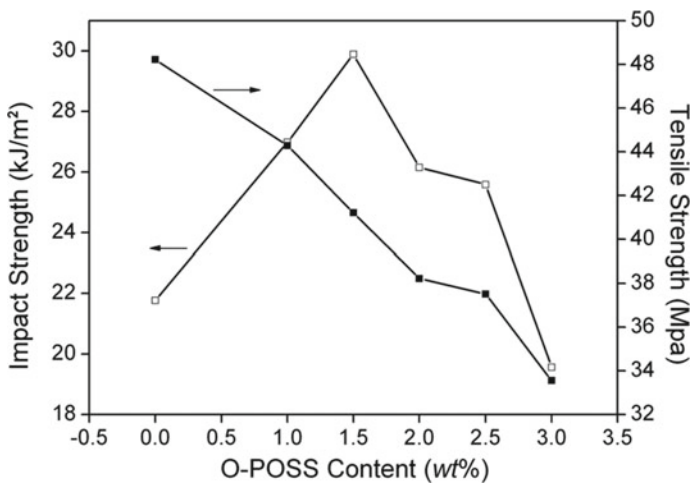

Fig. 4 Relationship of impact strength, tension strength, and O-POSS content [47]
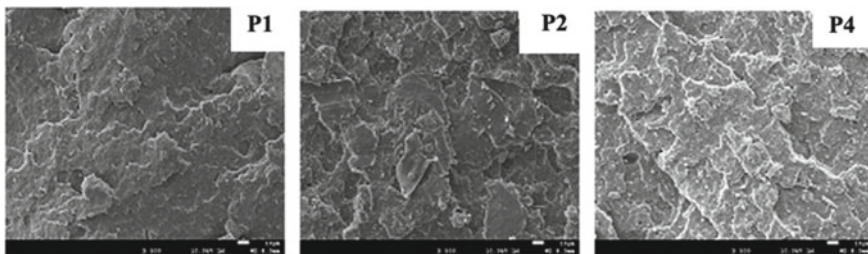

Fig. 5 SEM photographs of impact breaking surface of P1, P2 and P4 sample [47]

(Fig. 5 P2) by weight of O-POSS showed a toughness characteristic because of the plasticizing effect. An obscure structure was noticed due to poor compatibility in the morphological observation of the samples containing 2 wt% O-POSS, and it was assumed that there was a fall in impact strength due to phase separation. The DMA test was applied to the $20 \times 5x0.8$ mm^3 samples; extremely small variations in glass transition temperature (T_g) values were obtained due to the small amounts of O-POSS additive used [47].

In another study, Du et al., using similar production methods, produced PVC/chlorinated polyethylene (CPE) blends in different mixing ratios and nanocomposites by mixing 3, 5, 7, and 10 wt% methylacryloylpropyl-POSS (MAP-POSS) into 90–10 wt% PVC/CPE blend. Then, nanocomposite sheets of 1 mm and 5 mm thickness were subjected to tensile, impact, and DMA tests. Table 1 summarizes the mechanical test results, revealing that the blend with the highest impact strength is C20 coded blend containing 20 wt% CPE, and the nanocomposite with the highest impact strength is C10M10 containing 10 wt% MAP-POSS. Furthermore, the impact strength of nanocomposites was shown to rise as the amount of MAP-POSS increased in the blend systems. As a result of the SEM observations made on the impact samples, it was deduced that the C10M0 sample without MAP-POSS showed toughness characteristics.

In contrast, the samples containing 7 wt% MAP-POSS showed a layered and uncertain structure. Contrary to the impact strength results, it was concluded that the amount of MAP-POSS decreased the tensile strength. DMA tests revelaed that the storage module increases when a small quantity of MAP-POSS is added but drops when the amount of added MAP-POSS is increased. This was due to the low amount of MAP-POSS filling the free space between PVC and CPE and even partially crosslinking with PVC and CPE molecules. Due to filler effects and the crosslinks they form, the low amount of MAP-POSS addition improves the modulus value by preventing chain movements and increasing the friction force between the PVC and CPE chains. It was concluded that when the number of MAP-POSS in the nanocomposite increased, MAP-POSS molecules that could not crosslink with the matrix developed, lowering the modulus through a plasticizing effect [48].

Gao et al. produced six different nanocomposites using PVC and 3-chloropropyl-POSS (CP-POSS). In the PVC matrix, the CP-POSS content was 3, 5, 7, 9, and 11% by weight. The T_g values and mechanical properties were investigated via DMA and electronic tensile machines, respectively. At the same time, an XCJ-40 impact tester

Table 1 Data of impact strength and tensile strength of blends [48]

Sample no	C0	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/m^2)	6.90	8.01	8.91	11.42	12.28
Tensile strength (MPa)	20.36	14.28	11.58	10.44	9.55

was used to perform the notch impact test. DMA results showed that T_g values of CP-POSS/PVC blends increased upon addition of CP-POSS to PVC, but this increment was only by 2–3 °C, with the maximum T_g being 73.3 °C for the P3 sample having 3 wt% CP-POSS. The molecular interaction of PVC and CP-POSS accounts for the little increase in T_g. PVC molecules can generate physical crosslinks with the multi-polar groups of the CP-POSS molecule. However, because the CP-POSS has a lower melting point and plasticizes PVC, the T_g only increases slightly. Mechanical test results shown in Fig. 6 depicts the impact strength and elastic modulus data. When the CP-POSS content is 3–11 wt%, the blends have superior impact strength and have the best value at 7 wt%, but the elasticity modulus has the lowest value at 7 wt%. As a plasticizing agent, the CP-POSS can raise the impact strength of pure PVC, but it also has some activity to increase elastic modulus when the content is greater than 9 wt%. Figure 7 shows SEM images of P0 (pure PVC with 0 wt% CP-POSS) and P7's impact cracked surfaces. Figure 7 shows that the P0 has a smooth fracture surface and a brittle break; this is the brittle material's breaking feature. P7's fracture behavior reveals several toughness traits, such as a rough fracture surface and numerous holes, which is the breaking character of tough materials.

The plastic activity of CP-POSS in blends and physical cross-connections between PVC molecules and CP-POSS are also compatible with their findings. The plasticization effect is predominant when the CP-POSS content is less than 7 wt%, and the impact strength increases.

Based on the analysis of the mechanical and morphological features of CP-POSS/PVC blends, it has been determined that 3-chloropropyl-POSS (CP-POSS) has good compatibility with PVC and has a plasticizing impact on PVC. When the content of CP-POSS is 7 wt %, it can strengthen impact strength and has the best value. However, when the CP-POSS content exceeds 7 wt%, the impact strength drops, and
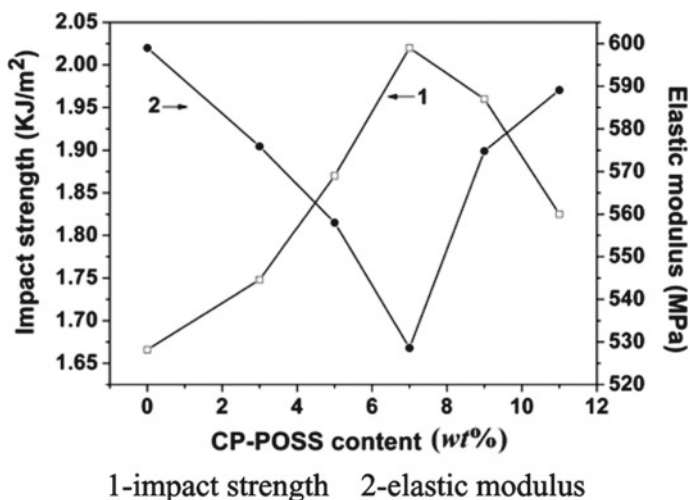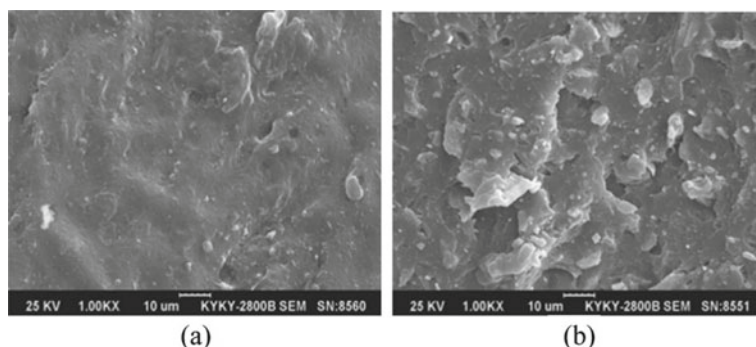

1-impact strength   2-elastic modulus

Fig. 6 Relationship between impact strength, elastic modulus and CP-POSS content [49]

Fig. 7 SEM photographs of impact breaking surface of P0 and P7 **(a)** P0, and **(b)** P7 [49]

the elastic modulus increases. For PVC, the CP-POSS can be utilized as processing support and an impact-resistant aid [49].

Yang et al. used a mixer and a laboratory two-roll mill to make nanocomposites of PVC/acrylonitrile chlorinated polyethylene styrene (ACS)/methylacryloylpropyl-POSS (MAP-POSS) containing 0, 1, 2, 3, 4, 5, 6 wt% MAP-POSS. PVC, ACS, and MAP-POSS were combined in a mixer before being milled at 185 °C on a laboratory two-roll mill. To determine dynamic rheological behavior and mechanical properties, 1 mm and 5 mm thick plates were pressed at 185 °C and subsequently cold-pressed for 10 min at 5 MPa. The researchers examined the mechanical and dynamic mechanical properties of these nanocomposites. Figure 8 depicts the relationship between the mechanical properties of PVC/ACS/MAP-POSS nanocomposites and their MAP-POSS content. According to Fig. 8, increasing the MAP-POSS ratio by up to 2% increases tensile strength, whereas increasing it by more than 2% drastically diminishes it. The impact strength results followed the same pattern as the tensile strength data. While the highest impact strength was attained at 3 wt% MAP-POSS ratios, there was an increase up to this rate before a decline. The cracked impact samples revealed that 3 wt% of the MAP-POSS additive made the structure ductile; however, when the ratio was increased to 6 wt%, the structure became brittle and had the reverse effect. The explanation was that the number of crosslinking increased as the amount of MAP-POSS increased. The maximum T_g value was obtained by DMA tests at a rate of 2 wt%, which was identical to the tensile test findings. T_g has developed a rising trend below 2 wt% and a falling trend beyond 2 wt%. In the storage modulus, comparable results were seen. Yang et al. concluded that the plasticizing action of free MAP-POSS and the balance of hydrogen bonds between MAP-POSS and PVC/ACS were responsible for the trend difference [50].

Palin et al. investigated the impact of POSS on a PVC matrix using two closed cages POSS types (Octvinyl POSS, VyPOSS, and glycidyl POSS, GlyPOSS) and two open cages POSS types (trisilanol heptaphenyl POSS, PhPOSSOH and trisilanol heptaisobutyl POSS, IBuPOSSOH). Nanocomposites were obtained independently and in an equal mixing ratio with all POSSs as a preliminary investigation
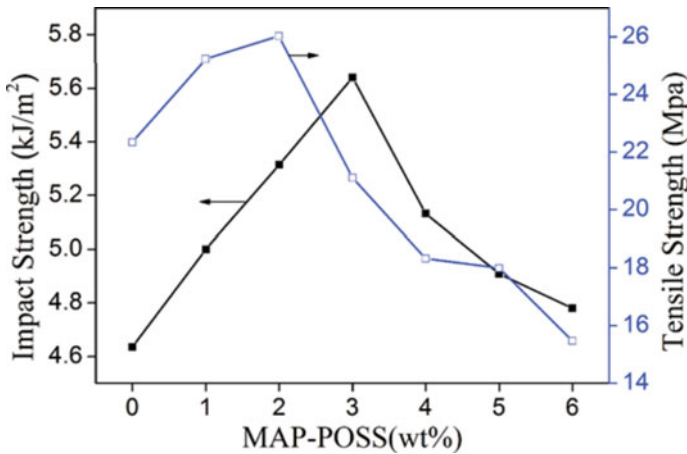
Fig. 8 Relationship of impact strength, tensile strength and MAP-POSS content [50]

to discover the optimal nano additive. As a result, VyPOSS and GlyPOSS were selected as outstanding contributions and are being explored further. VyPOSS and GlyPOSS were combined with X-type zeolite and carbonate-substituted hydrotalcite (CO_3-HTLC) nanoparticles. Hardness and mechanical properties were investigated to emphasize these additives' implications in final industrial applications. Mechanical test results showed that nano additives have almost no effect on properties like tensile strength and elastic modulus. On the other hand, the POSS improved the thermal stability of the nanomaterial-added samples without compromising their mechanical properties [51].

Silva et al. studied the tensile and dynamic mechanical properties of PVC/POSS nanocomposites containing 1 and 5 wt% chlorobenzylethylisobutyl POSS. Tensile test results are shown in Fig. 9, and it was found that the tensile strength of POSS modified samples was found lower than plasticized PVC compound. However, the addition of 1 wt% POSS improved the elongation at break value as compared to plasticized PVC compound. Furthermore, the weak interaction of POSS in the PVC matrix was observed due to the lack of the theoretically predicted increase in elastic modulus [52].

A research study was conducted by Soong et al. to investigate the application of polyhedral oligomeric silsesquioxanes to plasticize PVC. Traditional organic plasticizers for PVC, such as dioctyl phthalate (DOP), are relatively volatile, resulting in plasticizer loss and undesirable material degradation over time. Previous experiments have shown that methacryl-POSS (mPOSS) can plasticize PVC despite its low volatility due to its hybrid organic–inorganic composition. Using a lab-size extruder (DACA Instruments), melt blending was used to prepare various PVC/mPOSS and PVC/DOP binary blends, as well as PVC/mPOSS/DOP ternary blends. TA Instruments Q800 DMA was used to describe the thermomechanical behavior of the materials, and the results of DMA investigations are shown in Fig. 10. The
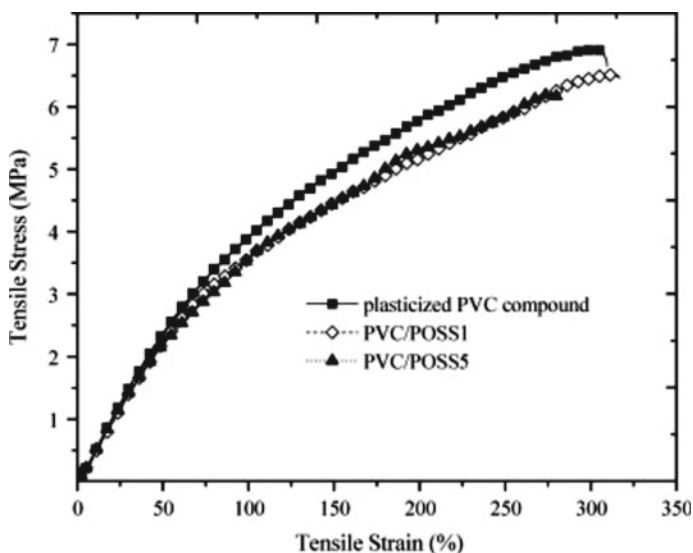
**Fig. 9** Stress/strain curves of plasticised PVC compound and PCV/POSS1 and PVC/POSS5 nanocomposites [52]

storage modulus, loss modulus, and tan δ curves for PVC/5 wt% DOP and ternary PVC/mPOSS/5 wt% DOP blends are shown in Fig. 10. PVC becomes more plasticized as its methacryl-POSS composition rises. Based on the tan δ peak value at 1 Hz, the addition of 25 wt% methacryl-POSS lowers the α-transition temperature of the PVC/5 wt% DOP from 77 to 59 °C. In DMA results, ternary blends produced with 20 wt% POSS and 20 wt% DOP showed lower α-transition temperature compared to pure PVC sample but higher value compared to 60 wt% POSS/40 wt% DOP binary blend produced without POSS. Also, DMA results revealed that the T_g of well-formed ternary PVC/POSS/DOP compounds could be decreased to near room temperature, and these materials have good ductility.

Figure 11 shows the uniaxial compression true stress–true strain curves of the ternary blends PVC/mPOSS/5 wt% DOP containing 5 wt% DOP at a strain rate of 0.001/s, which were tested using a Zwick mechanical tester (Zwick Roell Group). The compounds get more plasticized as the amount of methacryl-POSS in PVC increases. The materials change from glassy to leathery behavior, significantly reducing yield and flow stress. The mechanical characteristics of binary (PVC/DOP) and ternary (PVC/POSS/DOP) compounds formed with identical T_g values differed significantly. These findings suggest that POSS could be used to modify the mechanical properties of plasticized PVC [53].

Tomaszewska et al. investigated the modification of poly(vinyl chloride) (PVC) by polyhedral silsesquioxane containing both methacryl and octyl groups in another work (MeOctPOSS). Melt mixing was used to make PVC nanocomposites with

Fig. 10 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 [53]
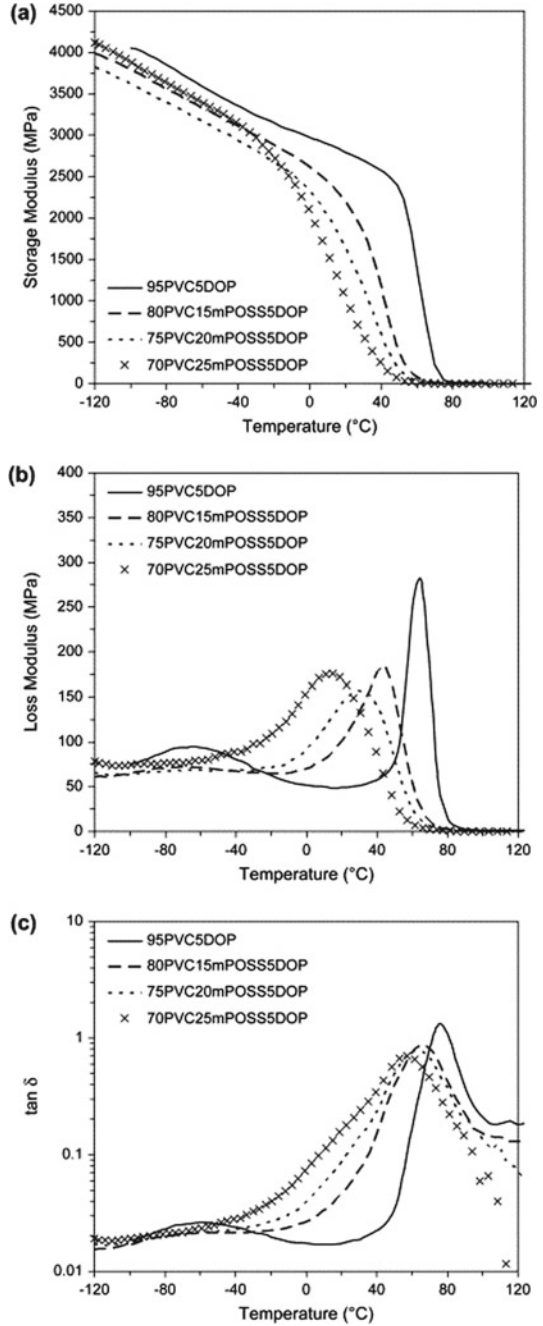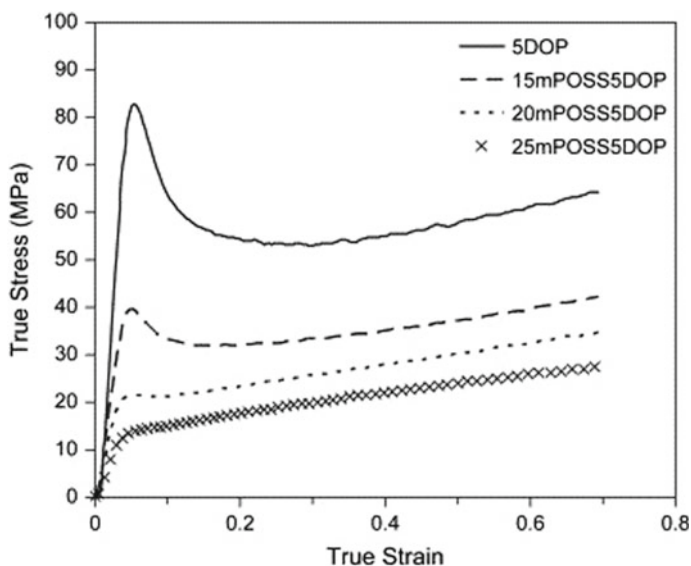
Fig. 11 True stress–true strain curves of compounds containing 5 wt% DOP and various amounts of methacryl-POSS. Testing was done in uniaxial compression at 0.001/s [53]

MeOctPOSS. MeOctPOSS concentrations ranged from 1 to 10 wt%. Scanning electron microscopy and energy dispersive spectroscopy measurements were performed to analyze the homogeneity of MeOctPOSS dispersion in the polymeric matrix. SEM pictures revealed that POSS dispersion in the PVC matrix was homogeneous. Based on the SEM findings, it is possible to conclude that the MeOctPOSS is equally distributed in the PVC matrix, regardless of additive concentration, and no agglomerates are present. The dispersion of silicon atoms in the PVC matrix was confirmed using EDS. As shown in Fig. 12a–d, all samples have a homogeneous Si-atoms distribution, which indicates the MeOctPOSS. Furthermore, no nano additives aggregates were visible to the naked eye, indicating that the nanocomposite production was proper.

The more concentrated the POSS additive, the denser the Si-atom distribution in the matrix, resulting in a brighter image. The mechanical analysis (tensile tests) was performed on an Instron 5985 universal tensile machine controlled by the BlueHill 2 program. The purpose of the tensile testing was to see if adding POSS to the PVC compounds changed their elastic characteristics. The plasticizing effect of the MeOctPOSS long chains was validated by uniaxial stress–strain tests that measured the elastic modulus of the PVC matrix as a function of the POSS content (Fig. 13). Moreover, the authors stated that adding POSS with long chains connected to the Si-cage lowers the modulus, especially at POSS concentrations over 2.5 wt%, with the most apparent consequence at 5 and 10 wt% [54].

Wang et al. investigated the influence of methacryl-functionalized polyhedral oligomeric silsesquioxane (MA-POSS) nanoparticles for a PVC homopolymer and a
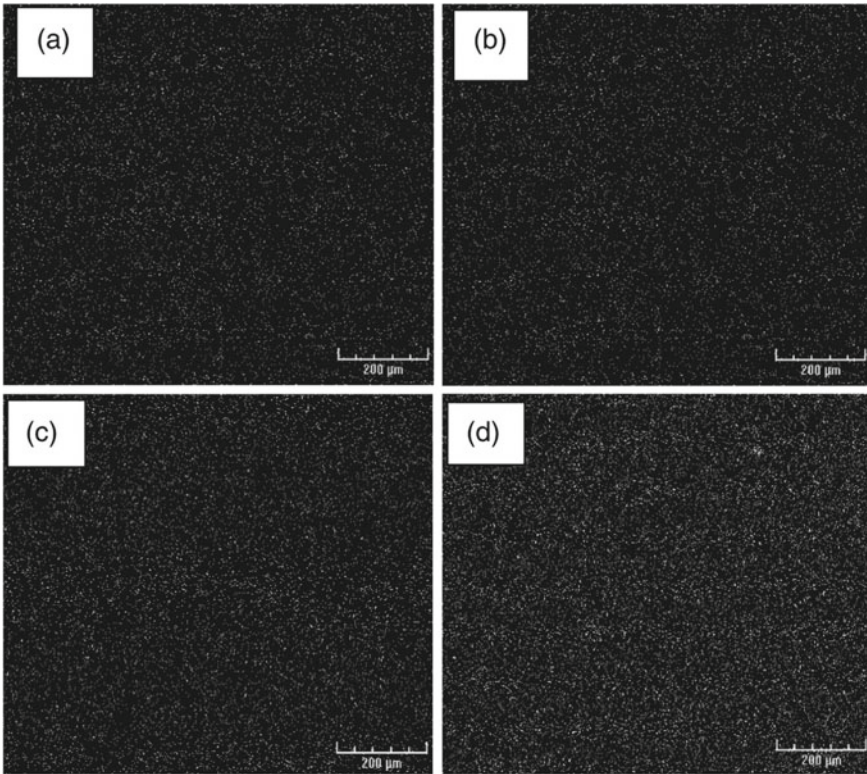
Fig. 12 Mapping of silicon atoms distribution of PVC composite: **(a)** PVC/1POSS, **(b)** PVC/2.5POSS, **(c)** PVC/5POSS, **(d)** PVC/10POSS [54]
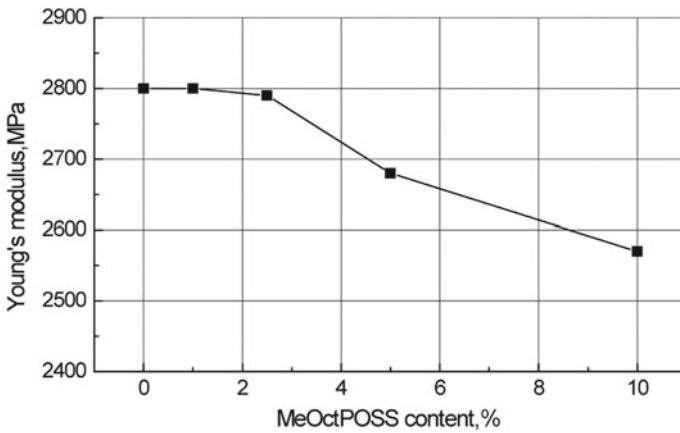
Fig. 13 The Young modulus of PVC nanocomposites as a function of MeOctPOSS contain [54]

PVC/dissononyl cyclohexane-1,2-dicarboxylate (PVC/DINCH) binary blend. They used MA-POSS as a plasticizer and thermal stabilizer. The PVC binary blends were prepared with 10, 20, 30, 40, and 50 wt% MA-POSS. On the other hand, ternary blends were prepared with 5, 10, and 15 wt% MA-POSS and PVC/DINCH blends. In this study, annealing at 100 °C for seven days was applied to the ternary blends. And the effect of MA-POSS amount of ternary blends on tensile properties before and after annealing was investigated. All the PVC/DINCH/MA-POSS ternary blends were found transparent and flexible; however, as the MA-POSS concentration was increased, their modulus and tensile strength both declined. Moreover, elongation properties increased both before and after thermal annealing. After seven days of thermal annealing at 100 °C, the elongation dropped, but the modulus and tensile strength increased (Fig. 14).

The DMA test results of ternary blends show that the T_g value increased with the increase in the amount of MA-POSS. Both DMA and tensile test results confirmed that MA-POSS nanoparticles were incorporated into the blends with complete miscibility. MA-POSS promises to be a viable candidate for substituting traditional plasticizers, such as di-(2-ethylhexyl)phthalate (DEHP), in PVC matrices [55].

3 Thermal Properties of POSS Reinforced PVC Nanocomposites

For many years, PVC has been investigated and used widely in industrial applications as an essential commercial commodity polymer. PVC and its composites, on the other hand, are limited in several applications due to intrinsic drawbacks such as low-temperature stability and brittleness. As a result, new PVC products with high quality and good qualities must be developed to generate high added values and boost PVC applications [58, 59]. Researchers have been working on enhancing the thermal stability and thermal behavior of PVC-based nanocomposites for a long time.

3.1 Glass Transition Temperature of POSS Reinforced PVC Nanocomposites

A differential scanning calorimetry (DSC) is one of the most effective methods for determining a material's thermal behavior. Different data can be collected as a result of DSC evaluation, such as melting temperature (T_m), crystallization temperature (T_c), and glass transition temperature (T_g). Glass transition temperature is among the specific properties of polymers. PVC is a polymer in amorphous structure due to the chlorine atom in its molecular structure, and its T_g value varies between 75–85 °C. A polymer's glass transition temperature is associated with its processability, whereas plasticizers make the processibility of polymers easier by reducing the glass transition
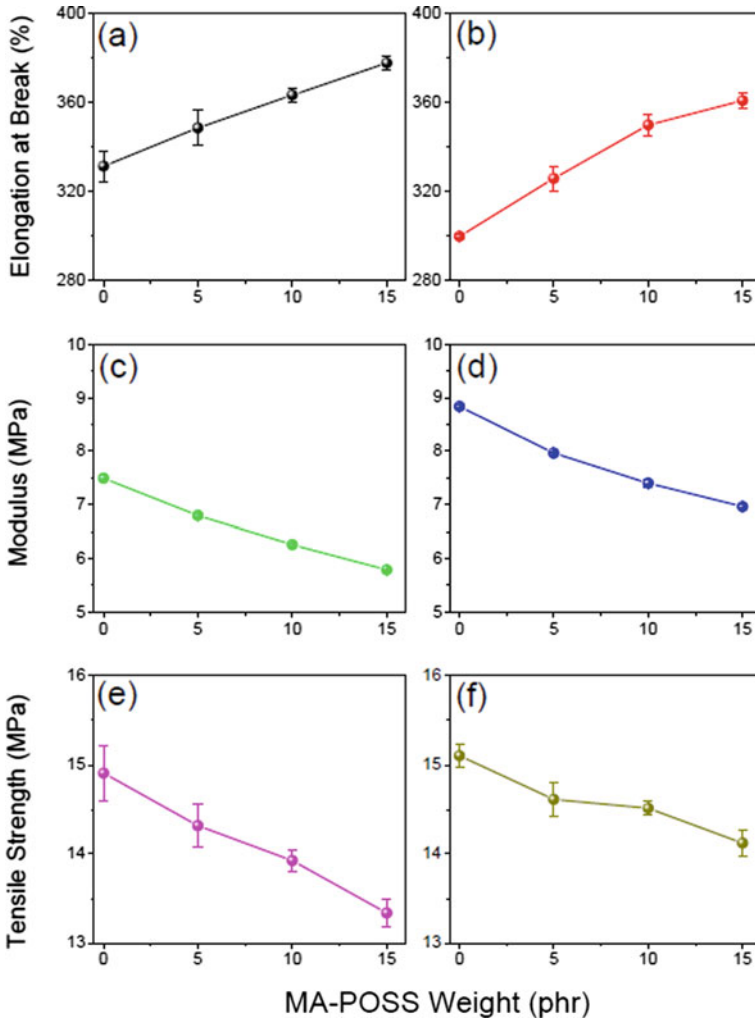
Fig. 14 Mechanical properties of PVC/DINCH/MA-POSS blends at various MA-POSS content (**a**, **c**, **e**) before and (**b**, **d**, **f**) after thermal annealing at 100 °C for 7 days: (**a**, **b**) elongation properties, (**b**, **d**) moduli, and (**c**, **f**) tensile strengths [55]

temperature. The literature shows that POSS nanoparticles added to PVC can reduce the plasticization time and balance torque values [50]. DSC analyses were carried out in many investigations to assess the Tg value of the nanocomposites. As can be seen from Table 2, PVC nanocomposites were prepared using various functional POSS nanoparticles, and the researchers used several DSC test methods to evaluate their T_g values. PVC/POSS nanocomposites with different POSS ratios were prepared using various methods, and the plasticizing effect of various functional POSS types on the PVC performance was investigated.

Table 2 Research studies using different POSS types and DSC test methods

Nanocomposites	Nanoparticle ratio (%)	DSC Method	References
PVC/PEG-POSS	0 20 40 50	• 25 °C−130 °C/10 °C/min 130 °C −5 min 130 °C−(−100 °C)/10 °C/min • Under a nitrogen atmosphere • Samples of approximately 10 mg	Yang et al. [58]
PVC/MA-POSS	0 10 20 30 40	• 25 °C−150 °C/20 °C/min 150 °C−(−90 °C)/20 °C/min −90 °C−200 °C /20 °C/min • Under a nitrogen atmosphere	Wang et al. [55]
PVC/ MeOctPOSS	0 1 2.5 5 10	• 30 °C−120 °C/5 °C/min • Samples of approximately 10 mg	Tomaszewska et al. [54]

The plasticizing impact of poly(ethylene glycol)–polyhedral oligomeric silsesquioxane (PEG-POSS) on PVC was studied by Yang et al. [58]. As the PEG-POSS ratio increased in the nanocomposites, PVC became more flexible, and T_g values decreased, as seen in Fig. 15. The T_g value of pure PVC was found at 72 °C, and T_g values were reduced to 57.6, 47.6, and 44.3 °C as PEG-POSS was added in amounts of 20, 40, and 50 wt%, respectively. This significant decrease in T_g values suggests that PEG-POSS has a specific plasticizing impact on PVC. These observed behaviors suggest that PEG-POSS is a potential plasticizer for PVC, especially at high PEG-POSS contents (50 wt%), consistent with prior literature [59]. The formation of hydrogen bonds was confirmed via FTIR analysis. The presence of hydrogen bonds would result in a substantial restriction on the mobility of polymeric chains, causing a drop in T_g values. PEG interacts with PVC polar groups when PEG-POSS is added, which is unfavorable for polar site interactions. PVC molecule chains would be separated from one another by the enormous bulk characteristic of POSS to a certain extent, giving them extra free volume. As a result, T_g value of PVC shifts to a lower temperature [58].

In another study by Wang et al., the plasticizing effect of methacryl-functionalized polyhedral oligomeric silsesquioxane (MA-POSS) nanoparticles on PVC homopolymer was investigated. PVC/MA-POSS mixtures were prepared by solution casting methods using MA-POSS nanoparticles in different ratios (Table 2). As a result of the DSC test performed at a heating rate of 20 °C/min, the T_g value for neat PVC was determined as 89 °C. The addition of 10 wt% of MA-POSS decreased T_g by approximately 26 °C compared to pure PVC. Increasing MA-POSS addition caused decreases in T_g values. The study emphasized that MA-POSS nanoparticle is a successful plasticizer for PVC [55].
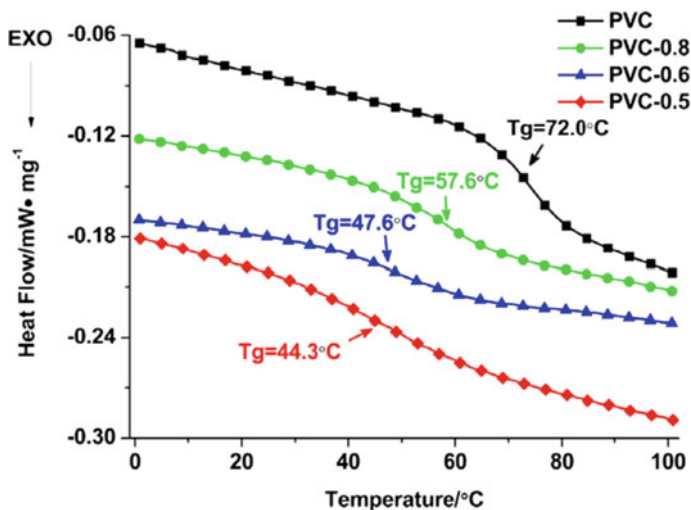
Fig. 15 Glass transition behavior of PVC and PVC/PEG-POSS nanocomposites [58]

Unlike previously investigated research studies, Tomaszewska et al. investigated the effect of polyhedral silsesquioxane containing methacryl and octyl groups (MeOctPOSS) at lower contents (e.g., 1–10 wt%) in PVC matrix. It was found that 1 and 2.5 wt% of MeOctPOSS ratios did not significantly alter the T_g values of nanocomposites (Fig. 16). However, when MeOctPOSS functional nanoparticles were introduced to PVC at 5 and 10 wt%, the T_g values of PVC nanocomposites significantly decreased. The interaction of PVC and POSS nanoparticles with octyl groups is suggested to be the cause of T_g reductions [54].

3.2 Thermal Stability Analysis of POSS Reinforced PVC Nanocomposites

Many industrial applications rely on the thermal stability of polymeric materials that are impacted by temperature changes. Thermogravimetric analysis (TGA) is one of the most widely used thermal analysis techniques in polymeric material characterization. PVC/POSS nanocomposites with different POSS ratios were prepared using various methods in several studies (Table 3). TGA measurements were performed to investigate the thermal stability of POSS reinforced PVC nanocomposites. The specification and testing parameters during the TGA analysis were also mentioned in Table 3. The inorganic structure (Si–O) of POSS nanoparticles reinforced the PVC nanocomposites thermally and made them more stable against heat transitions. Some of the research studies proved the positive impact of POSS inorganic core on the thermal stability of PVC nanocomposites.
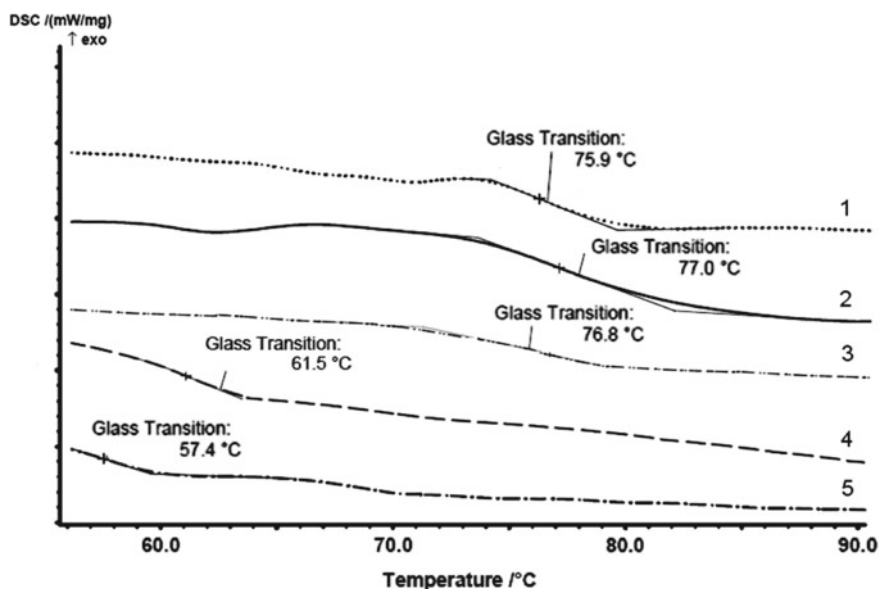
Fig. 16 DSC thermograms: 1-neat PVC, 2-PVC/1POSS, 3-PVC/2.5POSS, 4-PVC/5POSS, 5-PVC/10POSS [54]

Table 3 PVC-POSS studies and the TGA methods used in these studies

Nanocomposites	Nanoparticle ratio (%)	TGA Method	References
PVC/PEG-POSS	0 20 40 50	• 25 °C−680 °C−10 °C/min • Under a nitrogen atmosphere	Yang et al. [58]
PVC/MA-POSS	0 10 20 30 40	• 30 °C−800 °C−20 °C/min • Under a nitrogen atmosphere	Wang et al. [55]
P-PVC/VyPOSS P-PVC/GlyPOSS P-PVC/IBuPOSSOH P-PVC/PhPOSSOH	0.62	• 25 °C−800 °C−10 °C/min • Under a nitrogen atmosphere	Palin et al. [51]
PVC/POSS (chlorobenzyl methyl isobutyl POSS)	1 5	• 20 °C−600 °C−40 °C/min • Under a nitrogen atmosphere	Silva et al. [52]

In a previously discussed work, Yang et al. also investigated the thermal stability of PVC upon the addition of PEG-POSS into PVC. Thermogravimetric analysis (TGA) results showed that PEG-POSS showed a single degradation, while PVC showed a two-step degradation, as seen in Fig. 17. In PEG-POSS added PVC nanocomposites, the degradation step increased to three as the nano additive ratio increased. Step 3 was most clearly observed in the 50% PEG-POSS added nanocomposite (PVC-0.5). When the T_{max1} values of neat PVC and PVC-0.5 nanocomposite are examined, the PEG-POSS additive delays the HCl emission rate (Table 4).
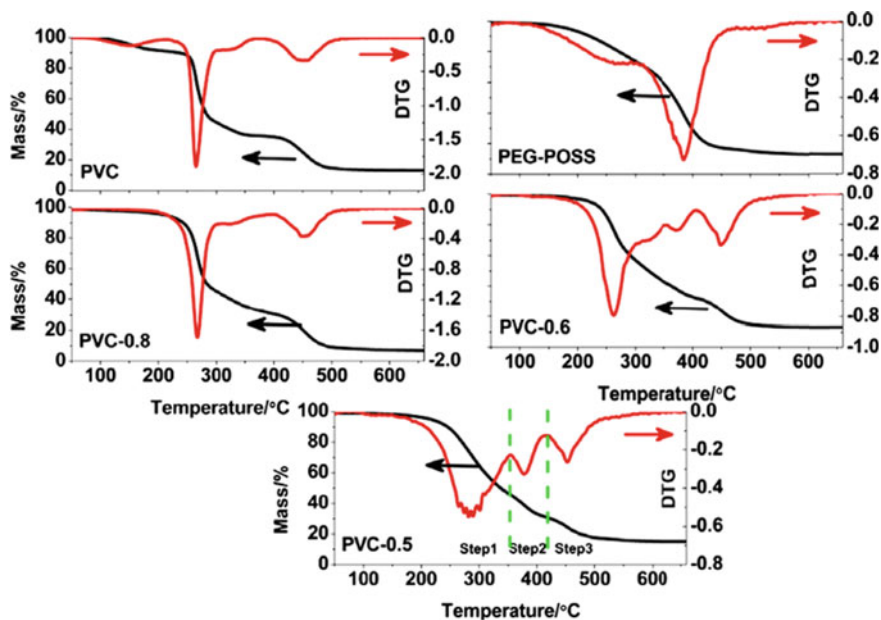

Fig. 17 TG traces of PVC, PEG-POSS and PVC/PEG-POSS nanocomposites [58]

Table 4 Thermogravimetric parameters of PVC and PVC/PEG-POSS nanocomposites[a] [58]

Sample	Step 1		Step 2		Step 3	
	T_{d1} (°C)	T_{max1} (°C)	T_{d2} (°C)	T_{max2} (°C)	T_{d3} (°C)	T_{max3} (°C)
PEG-POSS	–	–	196.5	384.9	–	–
PVC	252.5	265.3	–	–	412.4	443.5
PVC-0.8	252.6	267.2	–	–	427.5	445.2
PVC-0.6	249.3	264.3	–	372.2	428.4	449.3
PVC-0.5	253.2	285.7	–	378.1	432.7	452.5

[a] T_{d1}, T_{d2}: decomposition temperature at 5 wt% loss; T_{d3}: initial loss temperature of PVC in second decomposition process; T_{max}: maximum loss rate temperature of degradation product emission

Neat PEG-POSS exhibited single degradation, and the T_{max} value was 384.9°C. As the PEG-POSS ratio increased in the nanocomposite, T_{max} values increased but were lower than in neat PEG-POSS. Step 3 is due to the dehydrochlorination of PVC, T_{max3} values increased as the PEG-POSS ratio increased. It was emphasized that this was due to the non-pyrolysis residue of PEG-POSS [58].

In another study, Wang et al. investigated the impact of methacryl-functionalized polyhedral oligomeric siloxane (MA-POSS) nanoparticles on the thermal stability of PVC. TGA analyses were performed to assess the thermal stability of POSS reinforced PVC nanocomposites. The TGA curves of several PVC/MA-POSS blends, recorded from 25 to 800 °C at a heating rate of 20 °C/min, are shown in Fig. 18. Compared to pure PVC, pure MA-POSS had more excellent thermal stability. The first thermal decomposition temperature and char yield enhanced as MA-POSS content increased. The final step in the TGA curves corresponds to the pyrolysis of conjugated double bonds (for example, polyenes formed in the first step of PVC decomposition). Due to the retarding effect of MA-POSS nanoparticles on potential residual ash, the decomposition temperature and char yield rise with increasing MA-POSS concentration. Due to weak hydrogen bonds in the PVC/MA-POSS blends, TGA tests showed that adding MA-POSS nanoparticles could decrease the T_g of PVC and increase both its thermal degradation temperature and char yield while maintaining complete miscibility with PVC. To prevent DEHP from getting into touch with tissues or body fluids, MA-POSS has the potential to be an effective substitute for conventional plasticizers like DEHP. It might also be used as a blood bag [55].

Palin et al. used POSS nano additives with different cage structures and different R pendant groups. These POSSs were added to 0.62 wt% in plasticized PVC, and composites were prepared. The nano additives used, and their properties are shown in
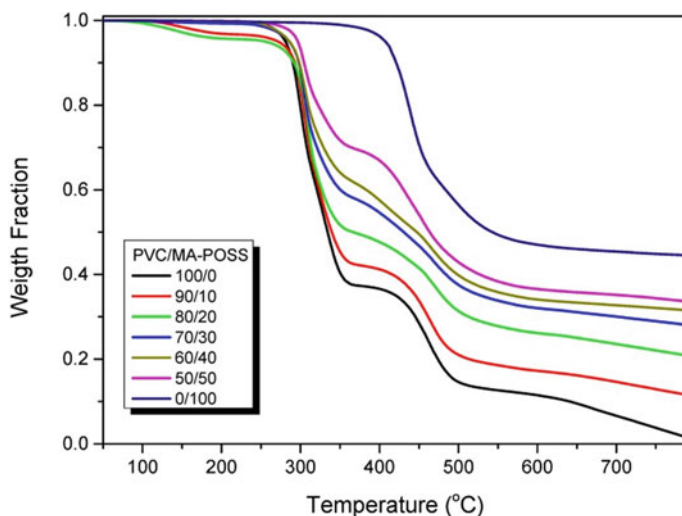

Fig. 18 TGA analyses of PVC/MA-POSS blends of various compositions [55]

Table 5. When the results were examined, all POSS additives improved the thermal properties of PVC. As can be seen in Fig. 19, the end groups rather than the cage structure play a more effective role in thermal stability. The best improvement was obtained in PVC-GlyPOSS nanocomposite, with an increase of about 11 °C in step 1 degradation [51].

Silva et al. prepared PVC-POSS nanocomposites with chlorobenzylethylisobutyl POSS in different ratios (1−5 wt%) to improve the thermal properties of plasticized PVC. TGA was used to characterize the thermal degradation of the plasticized PVC compound and the nanocomposites with the two POSS contents in an inert atmosphere. The results are displayed in Fig. 20. Similar to the plasticized PVC compound, PVC/POSS nanocomposites exhibited two-stage degradation. The first stage was attributed to the volatilization of hydrogen chloride molecules, followed by the formation of conjugated polyene sequences. The second stage is associated with the thermal cracking of the carbonaceous conjugated polyene sequences. The temperatures of the rapid degradation of each stage are represented by the two peaks in the first-derivative thermograms, representing the maximum weight loss rate of degradation. With the increase in POSS content, the thermogram did not show any

Table 5 Properties of POSS nano-additives used

Nanoadditive	Coding	Cage structure	R pendant groups
Vinyl-POSS	VyPOSS	Close	Vinyl
Glycidyl propyl ether-POSS	GlyPOSS	Close	Glycidyl propyl ether
Trisilanol heptaisobutyl-POSS	IBuPOSSOH	Open	Trisilanol heptaisobutyl
Trisilanol heptaphenyl POSS	PhPOSSOH	Open	Trisilanol heptaphenyl
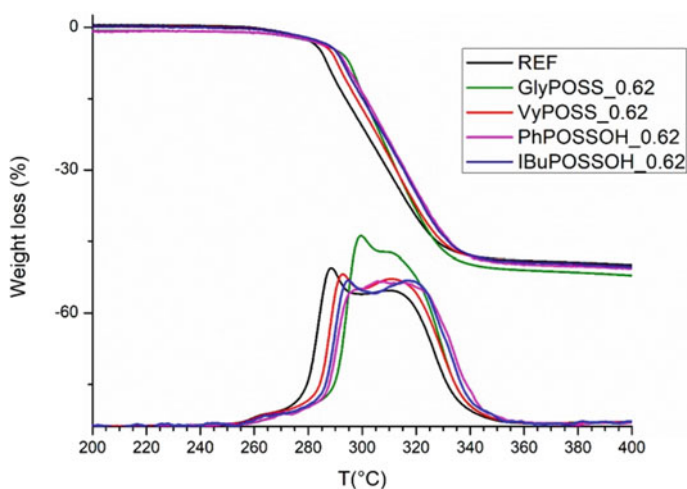
Fig. 19 TGA/DTG analyses of reference P-PVC (REF, black) and POSS formulated P-PVC [51]
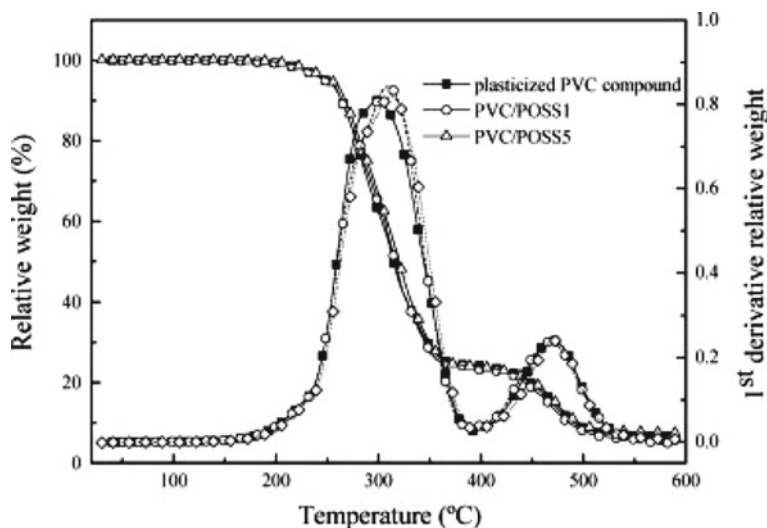
Fig. 20 TGA thermograms and first derivatives for plasticised PVC compound and PVC/POSS1 and PVC/POSS5 nanocomposites in inert atmosphere [52]

apparent alterations. This indicates that there are no significant interactions between PVC and chlorobenzyl ethyl isobutyl POSS [52].

4 Rheological Properties of POSS Reinforced PVC Nanocomposites

The rheological properties of polymers play a crucial role in the process and application of polymeric materials. POSS is typically used to modify the polymers; however, this process will also affect the melt viscosity and rheological behavior of polymers. This is because POSS can disperse at microlevel structure in the polymers.

4.1 Plasticizing Behavior of POSS Reinforced PVC Nanocomposites

Torque rheometers are used to determine the plasticization behavior of polymers. Torque rheometers measure the viscosity-dependent torque produced by the resistance to shear forces during the plasticization process of materials. By performing the tests at a certain temperature, data such as plastic time and equilibrium torque are obtained at the end of the test. In the plasticization process of PVC, the general

approach is that the resin is first divided into parts, further reduced by high temperature and mechanical forces. Regardless of the POSS type, the plastic time of PVC decreased with the increase of the POSS nanoparticles ratio [49, 51, 61, 62]. This situation is associated with the lower volatility, low viscosity, and organic/inorganic hybrid structure of the POSS nanoparticle [48].

Gao et al. prepared PVC/MAP-POSS nanocomposites by synthesizing the polyhedral oligomeric silsesquioxanes, which contain methylacryloylpropyl groups (MAP-POSS). Nanoparticles were added into PVC at 0, 2, 3, 5, 7, 9 wt%. The effect of the percentage content of MAP-POSS in nanocomposites was examined. Figure 21 shows the MAP-POSS ratio versus balance torque and plastic time curves. It was observed that the balance torque values of the PVC blends increased with the increase of MAP-POSS composition in PVC. On the other hand, plastic time has decreased. Since the methylacryloylpropyl group on the POSS end groups is compatible with PVC. Besides, MAP-POSS acted as a plasticizer for PVC [62].

In another study, Du et al. used MAP-POSS as nanoparticles for PVC, similar to the previous study. Chlorinated polyethylene (CPE) was additionally preferred as an impact modifier. The blend composition (PVC/CPE) was determined as 90/10, and nano-additive were added at different amounts of 0, 3, 5, 7, and 10 g. Rheological analysis showed that balance torque and plastic time values decreased as nanoparticle composition increased in the PVC-CPE blend. The plastic time value decreased by 81 s in the composite containing 10 g MAP-POSS compared to the pure PVC-CPE blend. It is suggested that MAP–POSS has plasticizing effect and lubrication in the melt. Thus, the nanocomposites' balance torque and plastic time decreased with increasing MAP–POSS content. MAP–POSS can also be a processing aid for PVC/CPE blend [48].
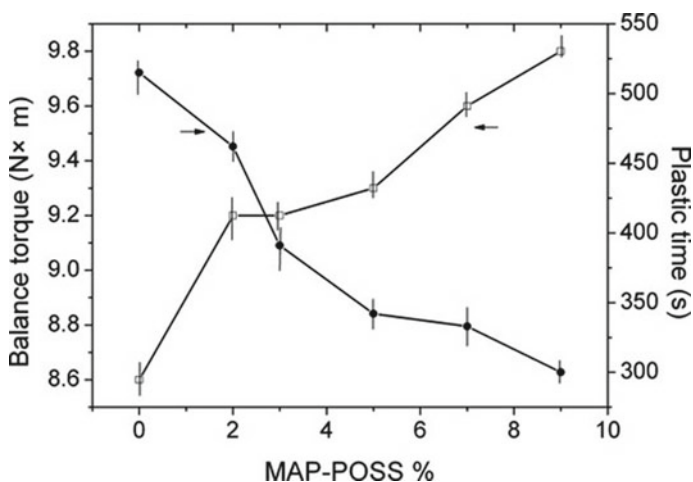
Fig. 21 Relationship of the balance torque, plastic time and the MAP-POSS content [62]

In another study, Yang et al. prepared the PVC/ACS/MAP-POSS nanocomposites. ACS has been added to the blend as a modified resin, which is compatible with PVC due to its sound processing and mechanical properties. ACS was added to PVC at a rate of 15 wt%. Using a torque rheometer, the plasticizing behavior of PVC/ACS/MAP-POSS nanocomposites was studied at 185 °C. Reduced plasticization times were observed with increasing MAP-POSS composition in the PVC/ACS. There was a slight increase in the balance torque values because MAP-POSS somewhat restricted the chain mobility of the blend and the possibility of weak hydrogen bonds between PVC/ACS [50].

In another study, a polyhedral oligomeric silsesquioxane that contains three chloropropyl groups (CP-POSS) was synthesized by hydrolytic reaction, and PVC/CP-POSS nanocomposites were prepared at 0, 3, 5, 7, 9, 11 wt% CP-POSS concentrations. As seen in Fig. 22, as CP-POSS increased in PVC, the plastic time of the nanocomposites decreased, and the balance torque values increased. The CP-POSS mixture has a low melting point, and the CP-POSS molecule, which is equivalent to nanometer particles, will fill the free volume between PVC molecule chains. So, the plastic time decreases with the increasing content of CP-POSS. But the chlorine atom of 3-chloropropyl on POSS can form a weak hydrogen bond with the PVC molecule. The hydrogen bonds hinder the movement of PVC chains. The friction force between PVC chains and CP-POSS increases, so the balancing torque increases with the content of CP-POSS [60].

Du et al. investigated the effect of polyhedral oligomeric silsesquioxanes containing octyl groups (O-POSS) on the properties of PVC. As the O-POSS content increased, the balancing torque and plastic time values decreased. The fact that the solubility parameters of PVC and O-POSS are relatively far from each other results in
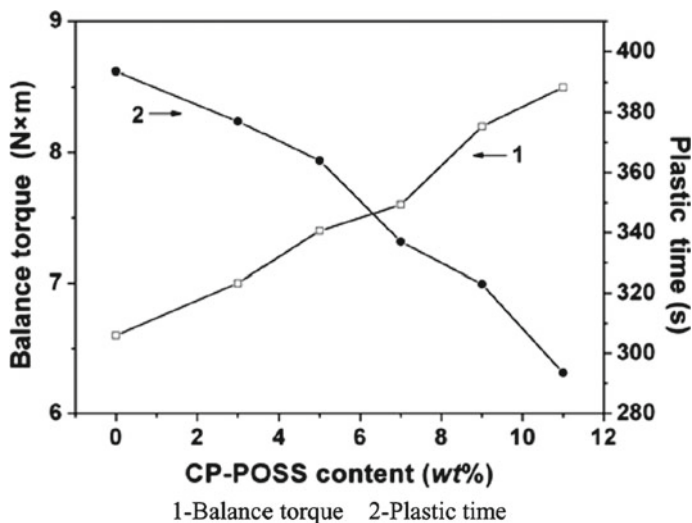

Fig. 22 Relationship between the balance torque, plastic time and the CP-POSS content [60]

poor compatibility between them. It has also been stated that the friction between the chains is reduced. Therefore O-POSS provides a plasticizer and lubricant effect [47].

As a result, balance torque values decreased as the O-POSS ratio increased [47] and increased as the CP-POSS ratio increased [48]. Balance torque was associated with weak hydrogen bonds due to compatibility between polymer and nanoparticle and crosslinking structure formed by the effect of temperature by Gao et al. [60]. These hydrogen bonds and crosslinked structures limited the movement of PVC molecules. O-POSS exhibits incompatible with PVC; however, CP-POSS and MAP-POSS showed good compatibility. With the increase of MAP-POSS ratio, balance torque values of mashed PVC and PVC-ACS nanocomposite increased [50, 60], while balance torque values of PVC/CPE nanocomposite decreased [48]. According to the studies, the plasticizing effect of POSS nanoparticles has been clarified regardless of whether they are compatible with the PVC. It has been observed that POSS nanoparticles with different end groups provide a plasticizer and lubricant effect for PVC. In addition, it was found that MAP–POSS can also be used as a processing aid for PVC/CPE blend [48].

4.2 Dynamic Rheological Behavior of POSS Reinforced PVC Nanocomposites

Oscillation rheometers are used for dynamic rheological measurements. In these rheometers, frequency, temperature, and strain sweeps can be made, and different modules can be studied. In frequency sweep experiments, the storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) of the melts are measured. The storage modulus (G') of material gives information about its elastic behavior. The loss modulus (G'') is related to the energy dissipation. The change in storage modulus may be due to the difference in hardness and interaction between polymer chains [48, 60]. Some of the research studies are summarized in Table 6.

Du et al. prepared PVC-based nanocomposites with polyhedral oligomeric silsesquioxanes containing octyl groups (O-POSS). The properties of six different

Table 6 PVC-POSS studies and the rheological test methods used in these studies

	Test method	References
PVC/O-POSS	Frequency sweep experiments: 25 mm in diameter at 185 °C, the frequency ranges from 0.1 to 100 Hz, strain is 1.25%	Du et al. [47]
PVC/CPE/ MAP-POSS	Frequency sweep experiments: 25 mm in diameter at 185 °C, the frequency ranges from 0.1 to 100 Hz, strain at 1.25%	Du et al. [48]
PVC/ACS/ MAP-POSS	Frequency sweep experiments: 25 mm in diameter at 185 °C, the frequency ranges from 0.1 to 100 Hz, strain at 1.25%	Yang et al. [50]

PVC nanocomposites at 0, 1, 1.5, 2, 2.5, 3 wt% were investigated, and the prepared nanocomposites were abbreviated as P1, P2, P3, P4, P5, and P6, respectively. To determine the storage and loss modulus of nanocomposites, frequency scanning was performed between 0.1 and 100 Hz. The strain value was selected as 1.25%. As a result of the evaluations, it was concluded that the modulus increases with the amount of O-POSS up to 2% in both G' and G'' values. It was observed that O-POSS restricted the chain mobility of PVC. Besides, the O-POSS addition increased the modulus values. It has been observed that these increments in rheological properties occurred faster in the low-frequency range. The authors stated that agglomeration of O-POSS beyond 2% resulted in weak mechanical properties such as modulus. The same phenomenon was observed for complex viscosity values. Stress relaxation tests were also performed at 185 °C at a 10% strain value. At higher content of O-POSS, the shear stress decreased; however, the time to reach the balance stress increased (Fig. 23). Below this ratio, these results are the opposite. By increasing melt elasticity, shear stresses increased, and more time was needed to reach equilibrium stress [47].

Du et al. investigated the rheological properties of MAP-POSS (different amounts of 0, 3, 5, 7, and 10 g) incorporated PVC-CPE blends, including 10 g of CPE. Figures 24 and 25 show the logarithmic plots of G' versus and G" versus frequency (Hz) of PVC/CPE/MAP–POSS nanocomposites at 185 °C, respectively. The PVC/CPE blend exhibited lower storage and loss modulus in the presence of MAP-POSS. The authors observed that the addition of MAP-POSS in low amounts showed a plasticizing and lubricating effect on PVC-CPE molecular chains. On the other hand, both storage and loss modulus increased as the MAP-POSS ratio increased in PVC-CPE blends. It was reported that hydrogen bonding occurred between the oxygen atom of the carbonyl group on MAP-POSS with -HCCl- on PVC and CPE molecules. G' and G" of the blend increased with the incorporation of MAP-POSS due to the
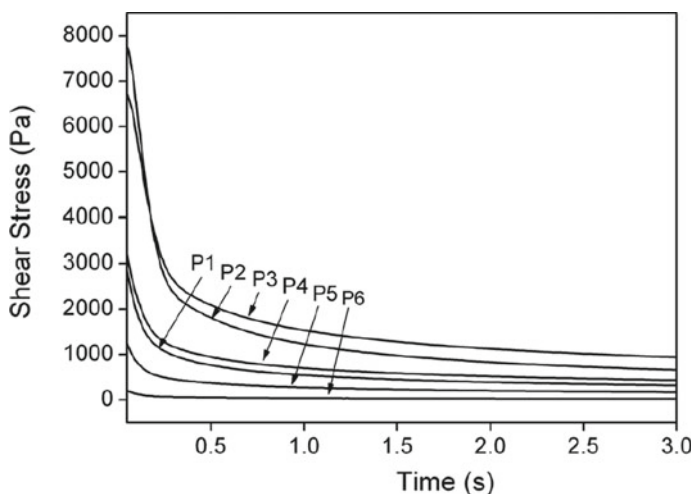

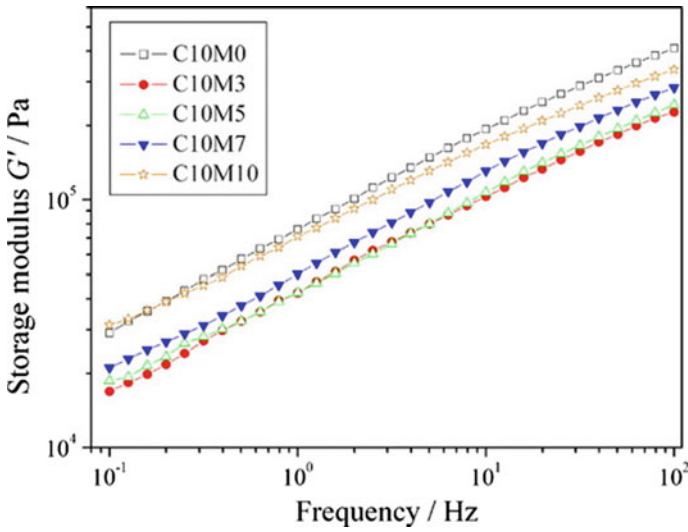**Fig. 23** Stress relaxation of PVC/O-POSS nanocomposites [47]

Fig. 24 Relationship between G′ and frequency of PVC/CPE/MAP-POSS melts [48]

restriction of free rotation and movement of molecular chains. When the complex viscosities were compared, decrements were observed with increasing frequency, while increments were observed with increasing MAP-POSS content. However, the complex viscosities were found lower than the neat PVC-CPE blend [48].
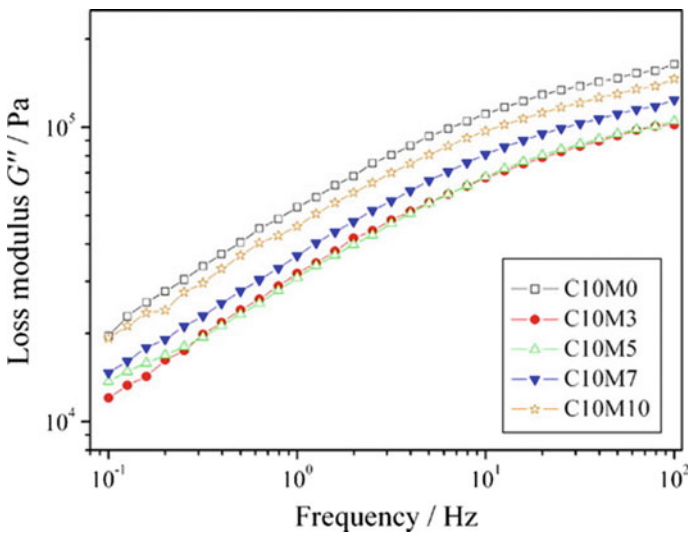

Fig. 25 Relationship between G″ and frequency of PVC/CPE/MAP-POSS melts [48]
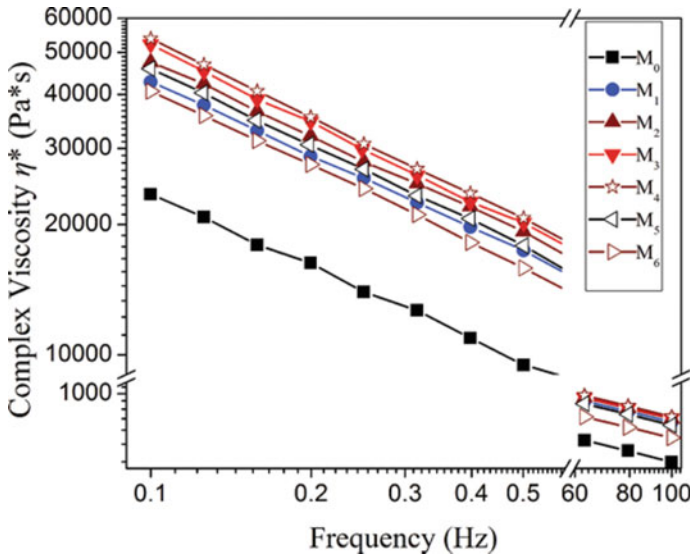
Fig. 26 Relationship between η* and ω for PVC/ACS/MAP-POSS [50]

Yang et al. prepared PVC/ACS nanocomposites consisting different content of MAP-POSS. Frequency sweep measurements were carried out at 185 °C. The storage and loss modulus and complex viscosity values of all MAP-POSS incorporated PVC/ACS nanocomposites were higher than the PVC/ACS. The maximum storage modulus value was obtained in 4 phr MAP-POSS added nanocomposites. On the other hand, rheological properties decreased as the POSS content increased. Complex viscosity values also showed a similar behavior with the modulus values (Fig. 26). While the complex viscosity values increased up to the addition of 4 phr MAP-POSS, the complex viscosity values decreased at higher MAP-POSS contents. This was attributed to the lubricating effect of MAP-POSS for PVC/ACS blends [50].

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