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PREPARATION METHODS AND PROPERTIES OF PVC BASED NANOCOMPOSITES

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Abstract. Polyvinyl chloride, or PVC, is a thermoplastic polymer that has found broad use in industrial settings. Numerous characteristics, including high tensile strength, biodegradability, extensive surface area, chemical stability, low weight, durability, affordability and availability, contribute to PVC's potential. Pure PVC's low thermal stability and brittleness, however, prevent it from being widely use; as a result, PVC modified with metal oxides and carbon nanofillers could significantly expansion its mechanical strength, thermal stability, biocompatibility, surface area, conductivity and other properties. Additionally, the great performances of nanocomposites in a variety of fields are ascribed to the reformed properties that arise from the chemical and physical interaction between the polymer and functionalized nanofillers as well as the nanofillers' good dispersion ability on the polymer matrix. In order to aid future advancements in this sector, this work attempts to provide an overview of the characterization and preparation of nanocomposites of PVC.

Keywords: *Polyvinyl chloride, nanocomposite, nanoparticles, modification.*

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1. Introduction

For providing synthetic and methodological improvement, polymers are crucial. Because of its low cost, strong mechanical strength, good fire retardancy, corrosion resistance, anti-chemical qualities and durability, polyvinyl chloride (PVC) emerged as the third largest synthetic thermoplastic polymer (Abdullah & Nage, 2011). PVC contains 58% chlorine and 42% hydrocarbon, which can be produced by free radical polymerization of vinyl chloride monomer in a variety of ways (Mahmoud & Al-Ghamdi, 2011). Challenges of using PVC in a variety of applications are revealed by its lower glass transition temperature, which results in weaker heat stability. One PVC's glass transition temperature is decreased by strong polar interactions within its molecules (Huang & Wang, 2009).

Bulk materials usually have distinct crystal structures and are sustainable systems. For a nanoparticle to be mechanically or structurally stable, its surface free energy must be low (Belov *et al.*, 2011). This situation can lead phases that are unstable in bulk materials to be highly stable in nanostructures (Bettio & Pessan, 2012). For making PVC nanocomposites, which combine the advantages of PVC and nanoparticles, nanoparticles are exposed to a PVC matrix. PVC nanocomposites thus show advanced properties, which increases their interest in polymer research (Olad *et al.*, 2013).

Chemical modification, particle content and integration all influence these nanocomposites' properties. The dispersion of integrated nanoparticles on the polymer matrix is the first determinant of PVC nanocomposites' performance (Liu *et al*., 2013b). These new nanoparticles include metal oxides, such as ZnO, Fe_2O_3, TiO_2, CuO and others and carbon allotropes, such as graphite, graphene, reduced graphene oxides and carbon nanotubes (CNTs) (Ren *et al*., 2005). By strengthening these particles, PVC can have uses in a greater variety of applications. These include water treatment, electric storage, humidity sensors, packaging and antimicrobials; their mechanical, electrical and thermal stability are examined in this research (Kemal *et al*., 2011).

Because of their superior qualities over traditional composites, nanoparticle systems have been seen to be quite interesting. The properties of polymers are more manipulated by lightweight nanoparticles, which can occasionally result in a favorable combination of properties (Al-Hartomy *et al*., 2011). Research on the application of nanoparticles in the making of nanocomposites has accelerated because of advancements in their synthesis. In different kind of displays, nanocomposites composed of polymers and nanoparticles have been shown to be linked (Liang *et al*., 2004).

PVC has lots of great properties, including high tensile strength, biodegradability, large surface area, chemical stability, low weight, durability, affordability and availability (Pagacz & Pielichowski, 2013). However, its brittleness and low thermal stability prevent it from being widely accepted in a variety of application fields. As a result, researchers developed a number of modification techniques (Feldman, 2012). For example, PVC mixtures with metal oxides and carbon nanofillers might significantly enhance mechanical strength, conductivity, surface area, biocompatibility, thermal stability and more (Liu *et al*., 2012a). On the other hand, the mechanical and chemical stability of PVC materials was enhanced by the chemical and physical interaction between the polymer and functionalized nano-fillers as the nano-fillers' high dispersion capabilities on the polymer matrix (Wanjun *et al*., 2012). So, an overview of the characterization, synthesis and usage of PVC nanocomposites is the main aim of this work (Turhan *et al*., 2011).

The uses and application areas of nanocomposites have expanded as a result of advancements in the synthesis of nanocomposite materials (Gilbert, 2013). The ability of nanocomposites to readily improve the host material's physical characteristics by including the correct nano-sized material has increased their value (Kim, 2012). The appropirate choice of base material and nanofilling material is the main concern in the using of nanocomposite. The physical and chemical characteristics of these nanocomposite materials differ from those of metal nanoparticles and pure polymers (Salavagione & Martínez, 2011). Because of their exceptional qualities, research on polymer nanocomposites has garnered a lot of attention, today (Bao *et al*., 2006). Graphene/PVC nanocomposite is more thermomechanically stable than pure PVC or a mixture of PVC and multi-walled carbon nanotubes (MWCNTs), according to Hasan and his colleague (Gong *et al*., 2004). In his investigation of PVC/Al_2O_3 composites, T. A. Taha found that the Al_2O_3 nanoparticles reduced the optical energy gap of PVC while also lowering the Urbach energy of PVC. Few or no studies have looked into how SiC affects PVC's characteristics (Yao *et al*., 2024).

Mineral nano fillers have been added to organic macromolecular compounds, such as PVC, to create polymer nanocomposites with advanced characteristics and decreased weight and cost because of the minimal percentage of filler required (Yang *et al*., 2006).

The following nano fillers are typically used: Both the naturally occurring sodium montmorillonite (NaCMMT) and the organomodified version known as organofilic (oMMT) of montmorillonite (MMT), other mineral clays such as halloysite, kaolinite, hectorite, bentonite and laponite, $CaCO_3$ or calcium carbonate, silica and talc, LDHs or layered double hydroxides, carbon nanotubes (CNT), vermiculite, a mineral that resembles mica and a blend of several fillers (Chen *et al*., 2012).

A very high surface of interaction can result from a small amount of nano filler scattered throughout the polymer matrix (Park & Jung, 2012). That is why, we can generate several nanostructures of polymer-nano filler composites based on it: The process of inserting polymer macromolecules in between the filler layers makes intercalated nanocomposites.The filler's individual layers are completely delaminated and distributed across a continuous polymer matrix in exfoliated nanocomposites (Abdullah & Nage, 2011).

2. Preparation of PVC based nanocomposites

Will the prepared PVC/filler nanocomposites function better or worse? We can determine the answer to this question by analyzing their properties using characterisation techniques. The following sections of this paper illustrate the properties of the nanocomposite using a variety of techniques, including scanning electron microscopy, transmission electron microscopy, fourier transmission infrared spectroscopy, thermogravimetric and derivative thermogravimetric analysis (Mahmoud & Al-Ghamdi, 2011).

There are numerous methods for creating intercalated or exfoliated polymer nanocomposites, including melt mixing, solution dispersion and in situ polymerization (Huang & Wang, 2009). Thus the levels of exfoliation and delamination, the preparation method and the quantity of nano filler have an effect on the primary properties of polymer nanocomposites (Belov *et al*., 2011).

Vinyl chloride (VC) suspension polymerization reaction was carried out in the presence of layered double hydroxide intercalated with sulfate anions (LDH-DS). It is called in situ polymerization (Bettio & Pessan, 2012). This transmission electron microscopy (TEM) analysis demonstrated that these nano filler particles were evenly dispersed throughout PVC and partially exfoliated and intercalated. The same authors also employed hydrotalcite (HT) nanoparticles in the suspension polymerization of VC (Olad *et al*., 2013). Alkyl phosphate (AP) was used to modify the surface of this micro filler. Investigations were conducted into the characteristics of the resulting PVC nanocomposites (Karakus *et al*., 2010). In the VC suspension polymerization process, some researchers have used nano $CaCO_3$ or MMT (Sokhandani *et al*., 2013).

For creating copolymer nanocomposites, VC was also used in copolymerization reactions. Poly(VC-co-vinyl acetate VAc-co-maleic anhydride MA) nanocomposites were made via suspension radical copolymerization with y-methylacryloxypropyl trimethoxy silane premodified in the presence of fumed silica. The study illustrated a considerable development in the primary copolymer characteristics (Bonadies *et al*., 2011).

PVC nanocomposites are often made using organic solvents including tetrahydrofuran (THF), dimethylformamide (DMF), dioctylphthalate (DOP) and others (Awad *et al*., 2009). Functionalized SiO_2 nanoparticles and PVC were ultrasonically disseminated in THF, followed by the addition of mercaptopropyl trimetoxy silane and magnetic stirring, in a standard production of chlorotrimethylsilane (TMCS). This method is called solution technique (Peprnicek *et al*., 2006).

The MgAl layered double hydroxide lauryl ether phosphate (LDH-PK) suspension was stirred with a PVC in THF solution (Madaleno *et al*., 2010). To prevent LDH platelets from aggregating, the mixture was put into ethanol for quick precipitation. Using the LDH-PK, it is regarded as a unique exfoliation re-staking process (Chipara *et al*., 2012).

The coating that results from THF evaporation is stable through a wide pH range and can be used to prevent corrosion on a lot of metal surfaces (Salavagionr *et al*., 2012). A clear PVC nanocomposite film was produced in the same solvent by using titanosilicate nano filler. Another study which used nano filler in varying concentrations (0.05, 0.005, 0.0005 weight percent) is about to create casting films based on PVC_6 multi-wall carbon nano tube (MWCNT) (Afzal & Akhtar, 2012).

Another study investigate the effects of adding nano clay (NaCMMT and oMMT) to the plastisol micro suspension PVC_6 diisononyl phthalate. PVC nanocomposites were created by solution mixing polyaniline modified TiO_2 (PANI-TiO_2) nanoparticles (1-5 wt%). The interfacial adhesion between the components of the nanocomposite can be developed because of the filler particles' wonderful ability of dispersion (Al-Ghamdi *et al*., 2012).

The plastisol process was also used in a study that gained seed oil from epoxidized Ceylon iron wood (Mesua ferrera L.) as a PVC plasticizer. PVC and epoxidized oilswelled MMT (5 wt%) were used in an ex-situ process to create nanocomposites (Wang *et al*., 2004). Thermogravimetric analysis (TGA) revealed a significant improvement in the nanocomposites' thermal and processing properties compared to virgin PVC. TGA and Fourier transform infrared analysis (FTIR) demonstrate that the primary nanocomposites are fully stable after isothermal tests at various temperatures (Du *et al*., 2012).

PVC plastisol and carbamide organo-clay nanocomposites show excellent mechanical properties and lower emissions of harmful smoke during combustion. Dimethyl formamide (DMF) was used to dissolve graphene oxide (Go) in a study and PVC was then added to the resulting mixture (Boonmahittihisud & Chulaujit, 2012). After coagulating and thoroughly washing with methanol, the nanocomposite (containing 5 wt% Go) was dried. When compared to PVC, it had better mechanical and thermal qualities (Liu *et al*., 2013b).

A Haake torque rheometer, a microcompounder, a mono screw extruder, a twin-screw extruder and other tools are utilized to manufacture PVC nanocomposites using a mixing technique with various nano fillers (Abu-Abden, 2012b).

PVC composites made in a Haak torque rheometer were examined to see how the size of the SiO_2 particles affected their fusion and rheological characteristics (Sarfraz *et al*., 2012). When the filler particles were 25 nm in size, some aggregates were visible in scanning electron microscopy (SEM) micrographs. However, when the size of the SiO_2 particles decreased, the temperature at which thermal deterioration began to occur was moved to a lower temperature (Hamid *et al*., 2013).

Nano SiO_2 added to plasticized PVC through the melt mixing process can develope its mechanical properties (Sokhandani *et al*., 2013). Di-butyl phthalate and an antistatic plasticizer containing bis(2(-methoxyethoxy)-ethyl) phthalate doped with sodium perchlorate were combined to create nanoparticles (SiO_2, TiO_2) loaded anti-static PVC. The resulting PVC nanocomposites demonstrated reduced surface resistivity, strong heat stability and processibility (Zhang *et al*., 2013). PVC micro and nanocomposites made in a Haake torque rheometer were made with SiO_2 particles of different sizes. It was discovered that when the size of the SiO_2 particles decreased, the composites' fusing time and temperature also reduced (Hou *et al*., 2012a).

In main investigations on nanocomposites, oxide nano fillers including Al_2O_3, TiO_2, CuO and $CaCO_3$ are also used. PVC was melted and combined with nano Al_2O_3 modified using a silane coupling agent. The nano filler was evenly distributed through the PVC matrix, as seen by the SEM data. Improvements were made to a few important mechanical properties (Hou *et al*., 2012b). PVC nanocomposites were made by melt blending by TiO_2 nanorods and nanopowder with PVC powder. An investigation was interacted on the interfacial adhesion between TiO_2 nanorods and the PVC matrix. The addition of nanorods improved PVC's mechanical and photostabilization properties (Shimpi & Mishra, 2011).

Poly (acrylic acid) (PAA) and the terpolymer poly (butadiene-co-acrylonitrile-co-acrylic acid) (PBAA) were used to modify nano CaCO3. PVC powder was first blended with stabilizer lubricant to create the dry blend.The dry blend was turned into an internal mixture in a subsequent phase. Researchers looked at how surface modifications and $CaCO_3$ nano filler modified the mechanical and thermal properties (Abu-Abdeen, 2012a).

PVC powder is mixed with an impact modifier, a stabilizer and a nano filler chosen from CNT, CuO and Al_2O_3 to create a nanocomposite in accordance with a patent (Zhang & Wu, 2011).

3. Properties of PVC based nanocomposites

Both bentonite and hectorite-based organically modified clays have been used to create PVC nanocomposites. The tallow-triethanol ammonium ion was used to modify it. For this study, TGA, DSC and DMA were employed. Using a typical thermal technique that evaluated the evolution of HCl and color development using the yellowness index, the thermal stability of the PVC nanocomposite was evaluated (Becerra *et al*., 2013). As the amount of PVC_6 halloysite nanotubes (HNT) rises, so do the heat distortion temperature (HDT) and the Vicat softening temperature (VST). The PVC_6 HNTs nanocomposites are additionally distinguished by a decrease in peak heat release rate (PHRR), total smoke production and smoke production rate (Liu *et al*., 2012b).

Using TGA and heat flow micro calorimetry techniques, the effects of Ag nanoparticles on the thermal properties of mixtures of dodecylbenzenesulfonic acid-doped polyaniline (PAND)6 PVC have been examined. It has been demonstrated that adding more PAND to these nanocomposites developed their thermal stability (Cushen *et al*., 2013).

Numerous other investigations discovered that adding various nano fillers rised the thermal stability of PVC (You *et al*., 2012). In both the presence and absence of DOP, PVC nanocomposites were also made by melt blending the polymer with an organically modified clay. TGA was used to assess the thermal characteristics and it was found that the amount of DOP and nanofiller affected the thermal stability. The filler had an impact on the progression of the polymer degradation process, as it is proved by the much lower proportion of PVC nanocomposites that stayed at 600°C (Ahn *et al*., 2011).

PVC_6 polyhedral oligomeric silsesquioxanes with octyl groups (o-POSS) nanocomposites were examined for their shape and other characteristics. When the o-POSS amount is 1.5 weight percent, their impact strength can enhance by 8 kJ6 m^2. PVC can benefit from the use of this nano filler as an impact addition in small quantities (Vlasov *et al*., 2012). It was investigated that when a specific amount of nano silica is added to plasticized PVC using the melt mixing technique, the tensile strength and elongation at break drop while the Young's modulus and rip strength rise (Bokova *et al*., 2012).

Because of its atactic structure, PVC is amorphous. Its soft form may lengthen up to 60% before breaking, while its hard form can remain a tensile stress of 46-52 MPa before yielding. This polymer is an excellent matrix for creating nanocomposites with improved mechanical characteristics because of these and other qualities (Kong *et al*., 2012).

4. Conclusion

We can illustrate the following results based on the information that collected by many researchers: PVC nanocomposites with excellent qualities to those of raw PVC are formed by adding of nano fillers, mixtures of nano fillers and nano fillers with specific polymers in the PVC matrix. A considerable decreasing in the PVC degradation temperature and HCl release was provided by some of these additions, which function as HCl scavengers. Depending on the selected nano filler, combinations of nano fillers, polymer and nano filler mixtures and the method used in their preparation, PVC nanocomposites also show developed mechanical, rheological, photostability, barrier, antibacterial, flammability and thermal properties.

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