Morphology of the Conducting Poly-*N*-vinylcarbazole-coated Silica Gel Nanocomposites

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We report the effect of surface morphology on the conductivity of the poly-*N*-vinylcarbazole (PVK)/silica gel (SiO_2) nanocomposites as a function of SiO_2 weight percentage (%). The polymerization of PVK was initiated by a free-radical polymerization. The surface morphology of the prepared composite shows the incorporation of SiO_2 in the prepared PVK-SiO_2 (PS) nanocomposites. The conductivity increased from 9.2×10^{-5} S cm^{-1} to 9.6×10^{-4} S cm^{-1} with the increase in the percentage of silica gel from 5 to 30%. The nanocomposites show a percolation behavior having a threshold value between 15 and 20%.

Introduction

In recent years, polymeric nanocomposites gained increasing attention in wide range of industrial applications including coatings, electronics, and adhesives.[1-5] The physical properties of conducting polymers have been improved significantly through blending with one or more insulating materials,[3] and the results are called polymercomposites.[3] The physical properties of the resulting nanocomposites are substantially improved with respect to microcomposites. The reason for the improvement is the higher interfacial area between the polymer matrix and blending material in the nanocomposite and the surface morphology.[6,7] The composites with improved surface morphology and nanoscale roughness of the polymer films lead to change in its optical, physical and chemical properties.[8] Consequently, techniques with high sensitivity to the surface physical and chemical properties are required to reveal the nanoscale properties of nanocomposites.

Poly-*N*-vinylcarbazole (PVK) is one of the attractive semiconducting polymers for electroluminescent and photorefractive devices.[9-11] The chemical and thermal stabilities of PVK, combined with its excellent electrical properties, make it very useful in the electronic devices. The polymerization reactions of *N*-vinylcarbazole can be performed in bulk, in solution, in suspension or in precipitation.[12-14] *N*-Vinylcarbazole monomer is polymerized by radical and cationic initiation both in the vinyl group and in the benzene ring because of its ability to stabilize electron-deficient centers by resonance involving the nonbonding electron pair on the nitrogen atom in the carbazole ring.[15] When the PVK polymerization proceeds through the vinyl group, a colorless photoconducting PVK is generally formed. The formation of the conducting PVK with dark green color, in which the polymer chain is formed exclusively by bonds between benzene rings, is possible.[12-16]

It has been reported that blending polymer with inorganic materials is considered as a powerful method to produce new materials called polymercomposites or filled polymers. How-ever, due to the significant development in nanotechnologies in the recent years, nanoinorganic materials such as SiO_2, Al_2O_3 and TiO_2 have brought much attention to this research field. Therefore, the polymer composites filled with nanoinorganic materials are well recognized as polymer nanocomposites. Essentially, addition of the nanomaterials into polymers may lead to overcome the drawbacks of pure polymers and produce new materials, which are considered to be robust. Basically, there are three methods used to produce the filled polymer; (i) melt mixing, (ii) solution blending, and (iii) *in situ* polymerization. Due to the direct synthesis *via* polymerization along with the presence of nanomaterials, the *in situ* polymerization is perhaps considered to be the most powerful techniques to produce polymer nanocomposites with good dispersion of the nanoparticles into polymer matrix.

Tanahashi *et al.*[16] pointed out that the application of nanosized fillers demonstrated the potential to improve the general performance of thermoplastic polymers fundamentally. It has been shown that a considerable improvement of mechanical properties can be achieved by adding a low volume content of nanosized fillers, somewhere in the range of 1 - 5 vol %.[17-19] This is very important due to the high cost of nanosized fillers. However, when nanoparticles are used as fillers to prepare polymer nanocomposites, a homogeneous dispersion in the matrix is required. As the particles tend to aggregate, special techniques have to be developed to achieve a homogeneous dispersion. One solution is mechanical mixing using high shear forces for dis-aggregation whereas another technique is ultrasonic irradiation. Chemical methods can also be used, such as sol–gel processing[20,21] or surface modification[22,23] of nanoparticles to increase the compatibility between nanoparticles and organic phase. Nanosized fillers acting as a part of the microstructure and the interfacial interactions mainly control the properties of the materials. This opens a new way to prepare high performance polymeric materials.

Here we report the synthesis of PVK-SiO_2 (PS) nanocomposites varying the amount of target mass loading of SiO_2. The

PVK composites are formed by a free-radical-initiated chain polymerization in which mixture of monomers is polymerized in the presence of an aqueous solution of surfactant in aqueous medium. After obtaining the PS nanocomposites the morphological characterizations and electrical conductivity were studied depending on the amount of SiO_2.

Experimental

Materials. *N*-Vinylcarbazole (98%, Aldrich) was purified by recrystallization from absolute methanol, dried in vacuum at 30 ^{o}C. 2,2'-Azobisisobutyronitrile (AIBN, 98%, TCI) and sodium dodecylsulfate (SDS, 95%, TCI) was used as received without purification. Silica gel (SiO_2) which is a spherical with the average diameter of 6 nm (99.99%) was purchased from Alfa Aesar. All solutions were prepared in aqueous media using deionized water.

Preparation of nanoparticles by emulsion polymerization. It is a free-radical-initiated chain polymerization in which a monomer or mixture of monomers is polymerized in the presence of an aqueous solution of surfactant to form a product.[24-28] Three-neck round double jacket flask was charged with 0.1 g of SDS and 250 g of water. The aqueous solution of surfactant was mechanically stirred over 3 h at room temperature. *N*-Vinylcarbazole (10 wt % of toluene) dissolved in 1 mL of toluene containing the target mass loader of SiO_2 was added with drop wise to the reactor. And then, the resultant monomer emulsion was subjected to mechanical agitation at 700 rpm for 1 h. The reaction was then initiated by the addition of initiator (1 wt % of the monomer). The polymerization temperature was kept constant at 70 ^{o}C throughout the reaction (reaction time = 24 h) under nitrogen atmosphere. After predetermined time, the reaction mixture was cooled. And then, dialysis was carried out for 1 - 2 days in

order to remove the surfactant and initiator. The polymer nanoparticles were separated from the dispersion medium by centrifuging and dried in vacuum over night. During the centrifugation the unattached PVK is removed and the PVK-coated SiO_2 particles will remain as the residue. The target mass loading of SiO_2 in the composites varied from 5 to 30 wt %. The PVK homopolymer was synthesized under the same conditions for comparison purposes with the composites. The composites are abbreviated as PS-*x*, where *x* refers to the wt % of the SiO_2 powder used in the polymerization reaction.

Characterization. The powder morphology of the synthesized composites was investigated with SEM (XL-30 ESEM, Philips). A Hand Press (Model: SPECAC) instrument for pellets preparation was used. The powder obtained was made pellets by using stainless steel mold applying 10 ton/cm^2 pressure under vacuum for 10 minutes. The electrical conductivity was measured at room temperature using a standard Four Point Probe technique with a Keithly 224 constant current source and a Keithly 617 digital electrometer. The probes were placed on surface of the pellet. The thickness of the pellets was measured by using a micrometer. Calculation of the conductivity is as stated below: [22, 23]

$$\sigma = I \ln 2 / V\pi t \qquad (1)$$

where σ = conductivity, I = current in Ampere, V = voltage in Volts and t = thickness of the pellet in cm.

Results and Discussion

Surface morphology. The surface morphology synthesized PS nanocomposites were analyzed by SEM studies. The images for PS-10, PS-20 and PS-30 nanocomposites containing differ-
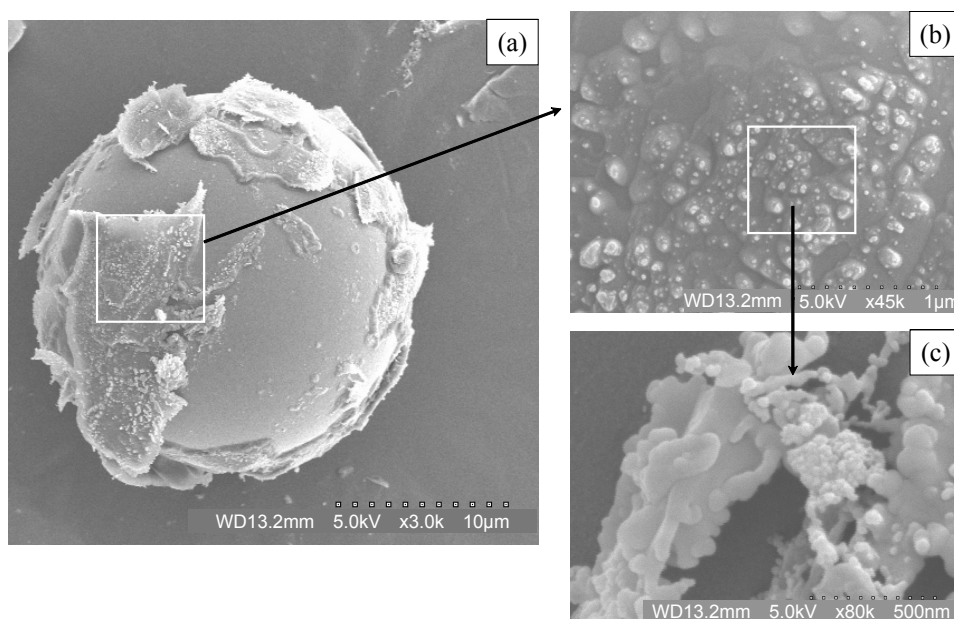
Figure 1. The surface morphology of the PVK/SiO_2 nanocomposites for the PS-10 (10% of SiO_2) obtained by SEM at 10 μm (a), (b) is showing a portion extended to show the surface modification at 1 μm, and (c) is more extended image to 500 nm. The image shows that PVK is coating the surface of SiO_2 particle.
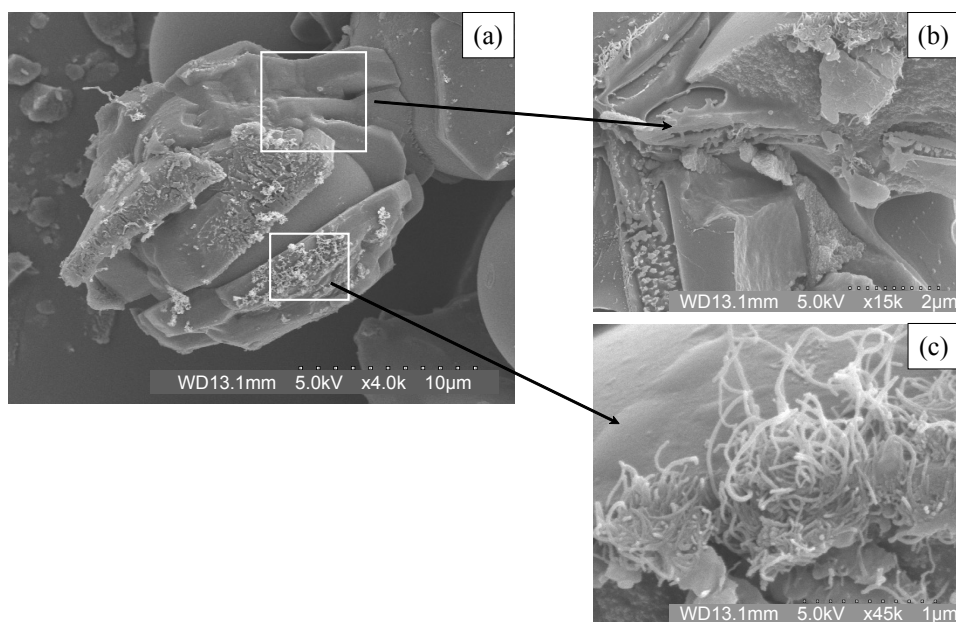
Figure 2. SEM image for the PS-20 nanocomposites obtained at 10 μm (a), (b) is showing a portion of which extended to show the surface modification at 2 μm, and (c) is at 1 μm.
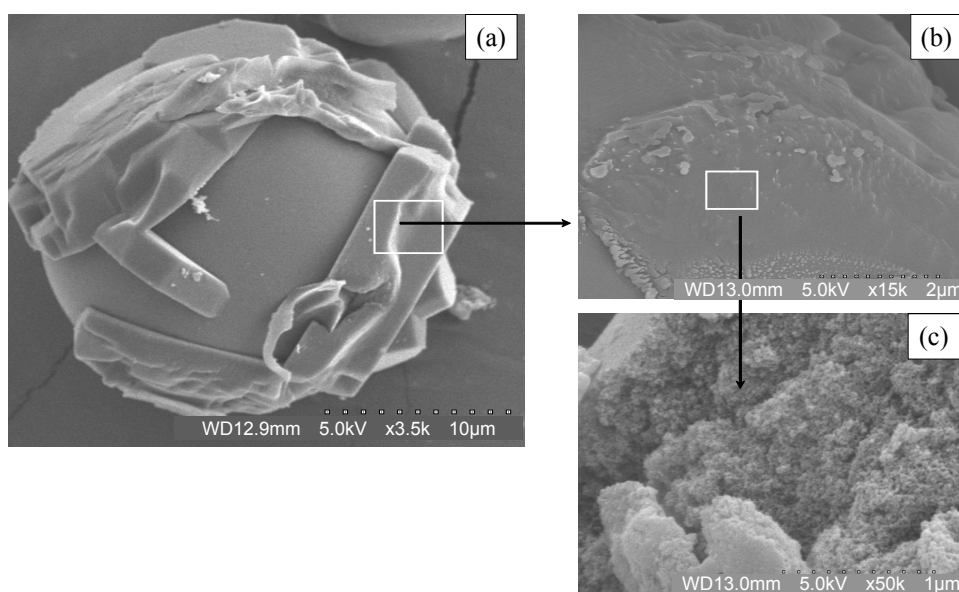
Figure 3. SEM image for the PS-30 nanocomposite obtained at 10 μm (a), (b) is showing a portion of which extended to show the surface modification at 2 μm, and (c) is at 1 μm.

ent amounts of SiO_2 are shown in Figure 1, 2, and 3, which present some typical data showing the formation of poly-*N*-vinyl-carbazole-silica composite. The square in the inside the figures are to show a clearer image of the surface of the PVK attached to SiO_2 particles. In PS-10 the coating of SiO_2 particles is not complete as shown in Figure 1(a); the polymer PVK forms patchy coating. It can be seen that the surface of SiO_2 is covered with PVK polymer. Figure 1(b) shows the extended SEM images of the PS-10 shows the structures of tiny particles in the form of clusters which are of irregular shapes. Further magnified

image in Figure 1(c) indicates the bulk morphology with needle/fibrillar structures here there are also seen in the figure. In PS-20 the coating of SiO_2 is higher than that of PS-10. The PVK portion covered on the surface of SiO_2 is extended and is shown as Figure 2(b). Figure 2(b) forms a layer like structures appeared in the form of stacking. Figure 2(c) is a further extended portion of 2(b) whish shows fiber-like structures. On increasing SiO_2 wt% the coverage by PVK on the surface of SiO_2 has become more heart. If we observe the SEM image for the PS-30 is given in Figure 3(a) and the extended portion for the image is shown in
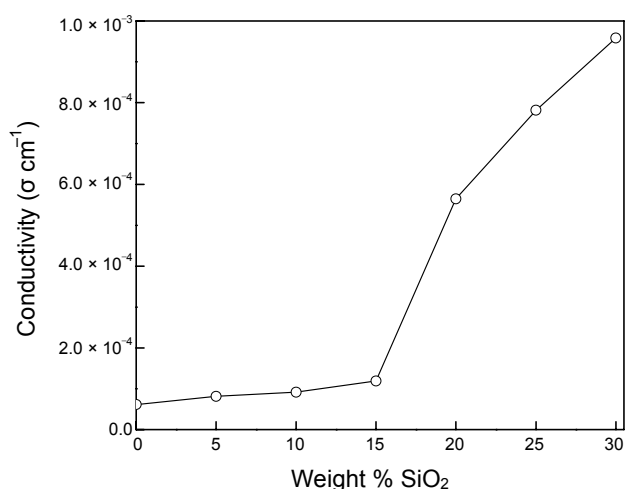
Figure 4. Conductivity of the PS nanocomposite pellets obtained at different weight percentage of SiO₂.

Figure 3(b) which shows a stacked flake like structures. But Figure 3(c) exhibits powder morphology differently from Figure 2(b) of PS-20.

It has been observed that the coating formed by PVK on the surface of SiO₂ nanoparticles increases with increasing SiO₂ content during the synthesis process which is evidenced in PS-20 and PS-30. We believe this type of coating is more pronounced with an increase in SiO₂ during the synthesis process. It means that dispersed coating of SiO₂ by the PVK polymer is well performed when the portion of SiO₂ is increased.

Conductivity study for PVK and PS nanocomposites. Our research is focused on the effect of morphology on the conductivity of polymer nanocomposite when a nonconducting filler is used as a target mass loading material. In this case PVK acts as a representative of conducting polymers and the conductivity obtained at room temperature in this study was 6.1×10^{-5} S cm^{-1}, while the target loading material of the SiO₂ was 6.8×10^{-10} S cm^{-1}. Figure 4 shows the conductivity of SiO₂ and PS at room temperature. The conductivity value for PS-10 is 9.2×10^{-5} S cm^{-1}, PS-20 is 5.7×10^{-4} S cm^{-1} and that of PS-30 is 9.6×10^{-4} S cm^{-1}, and thus there is a sudden increase in the conductivity as the fraction of SiO₂ increase as 20%. This may be due to the percolation behavior[29] in the PS nanocomposite.

The system has a threshold in PS-20 further increase in SiO₂ the conductivity passes the percolation limit, the sudden jump in the conductivity is probably due to well coating of SiO₂ by PVK. By the observation it was found that PVK synthesized in the present case has a gel form once the SiO₂ was introduced during the synthesis. And the synthesized nanocomposites will have powder form. This may facilitate the process of conductivity and so as the increase in the percolation behavior of the nanocomposites.

The percolation theory was applied to explain electrical conductive behavior of composites. Near the percolation threshold, the electrical conductivity of composites follows a power-law relationship: [30]

$$\sigma = \sigma_o (V_f - V_c)^s \qquad (2)$$

where σ is the electrical conductivity of the composite, σ_o is the electrical conductivity of the filler, V_f is the filler volume fraction, V_c is the percolation threshold, and s is a conductivity exponent. Because equation (2) cannot take into account either of particle shape, orientation, polymerparticle interaction or particle dispersion, the value of s is not a constant, but varies with particular composite systems. s and V_c have to be determined by curve fitting of experiment results. A recent review of analytical models for electrical conductivity of conductive polymercomposites[31] suggests that the majority of existing models dealt with simply shaped fillers, such as rod and close-to-spherical shaped fillers. The percolation behavior observed in this study is similar to the results obtained in the literature.[32] Previous experimental studies[32-36] suggested that as the conducting filler content gradually increased the composites underwent an insulator-to-conductor transition and a typical percolation behavior was observed. For the conducting polymer samples, the different parts of the composites are proposed to be the more ordered (metallic) regions and the disordered regions where localization becomes important. The percolating behavior of conducting polymers is expected to be modified from traditional insulator-metalcomposites as the ordered and disordered regions do not have sharp boundaries; a single polymer chain may be a part of both ordered and disordered regions.

The sudden increase in the conductivity is attributed to the morphology of PS composites. This behavior is attributed to the formation of multiple, continuous electron paths, or conducting network, in the polymercomposites with the filler content at or above the percolation threshold. The PS composites synthesized in this study have improved in conductivity and surface morphology as compared to each individual component. There is a considerable change in surface modification and the conductivity of base polymer due to the addition of SiO₂ which acts as reinforcing filler for the matrix and does not deteriorate the mechanical properties like other nonreinforcing fillers. This is mainly because the growing radical propagates further on the SiO₂ surface and cross-links into a microgel by the copolymerization of PVK.

Conclusion

SiO₂ based composites of PVK were obtained by polymerizing free-radical-initiated chain polymerization in which a monomer or mixture of monomers is polymerized in the presence of an aqueous solution of surfactant. The conductivity values of PS composites increased with the increase in SiO₂ loading in the composite and this is quite significant as compared to PVK and SiO₂. The nanocomposites show a percolation behavior having a threshold value between 15 and 20%. The increased conductivity can be related to the morphology of the PVK covering the SiO₂ surface. The morphological study from the SEM analysis shows the PVK patchy coating of composite with the increase in SiO₂, the patchy coating of PVK may be responsible for enhancing the conductivity. The PS nanocomposites particles produced by our method appear as powders. This powder can be used as a basic material for use in a variety of technological formulations such as low dielectric constant materials and filter material that can be easily handled and assembled

into various forms, such as pellets, ribbons, paste, *etc*.

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