FABRICATION OF ORDERED POROUS POLYMER FILM IN POLY- (*N*-VINYLCARBAZOLE)/MULTIWALLED CARBON NANOTUBE COMPOSITE

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1. Introduction

Carbon nanotubes (CNTs) are endowed with unique structural and electronic properties, and have extensive applications in many fields. However, the manipulation and processing of CNTs have been blocked by their insolubility in most common solvents and tendency to aggregate. Various attempts have been made to obtain homogeneous CNT dispersions in both aqueous and organic media [1,3].

In recent years, many researchers interested in studying the low-cost photovoltaic materials. Attempts have been made to study various organic materials and organic–inorganic hybrid structures. Among different polymeric materials, poly-(*N*-vinylcarbazole) (PVK) is widely used in light-emitting diodes, xerography and in general as an electro-optically active polymer because of its specific photo-physical properties [2,4]. One of the important advancements in this direction is the preparation of hybrid nanocomposite materials of these polymers with selective inorganic components [4].

In this study, the fabrications of regularly ordered structure in the PVK and PVK-MWCNT composite films are reported. The composites were prepared by the dispersion of pretreated multiwalled carbon nanotubes **(**MWCNTs) into the PVK solution in chloroform with varying amounts of MWCNT (1, 5, 10 and 15 w/w%). Highly ordered polymer films are produced by evaporating a solution of polymer dissolved in a volatile solvent under humid conditions [5].

2. Experimentals

2.1 Materials

N-Vinylcarbazole (98 %, Aldrich) was purified by recrystallization from absolute methanol, dried in vacuum at 30 ^{O}C. FeCl3 (97 %, Aldrich) was purified by chloroform.

All the other reagents of the pristine MWCNT (diameter = 110–170 nm, length = 5–9 nm, Aldrich), sulfuric acid (98 %, Aldrich), nitric acid (65 %, Aldrich), methanol (≥ 99.8 %, Aldrich), and chloroform (≥ 99 %, Aldrich) were used as-received without further purification. De-ionized (DI) water was used in this experiment.

2.2. Synthesis of Poly-N-vinylcarbazole

PVK was synthesized from *N*-vinylcarbazole monomer (NVK) and $FeCl_3$ used as an oxidizing agent. *NVK* (1g) was initially dissolved in 10 mL of chloroform and sonicated for 30 min. In a separate mixture, 1 g of the oxidizing agent was added to another 10 mL of chloroform, which was then filtered using filter paper. This filtrate was added slowly into the solution containing the monomer. After complete addition, the mixture was sonicated for 10 min and kept in a refrigerator maintained at 0-4 ^{o}C for 12 h. The mixture was then removed from the refrigerator to attain ambient conditions. When a suitable temperature had been achieved, methanol was added to the mixture. The precipitate was washed and then dried in an oven for 24 h at 60 ^{O}C.

2.3 Preparation of composites

For the composite films, about 100 mg of PVK and 1 w/w% of MWCNTs were taken in a beaker along with about 5 mL of $CHCl_3$. The solution were sonicated at room temperature for a long time (12h) to obain a homogeneous mixture. The same procedure was repeated for the 5, 10 and 15 w/w% of MWCNTs. For comparison, a patterned film by PVK alone was also obtained without adding the MWCNTs.

In this study, the PVK-MWCNT composites with various weight percentages of MWCNTs (1, 5, 10 and 15 w/w%) in PVK are abbreviated as PMT-1, PMT-5, PMT-10 and PMT-15, respectively.

2.4 Fabrication of ordered structures in the PMT composites

Fig. 1 shows the schematic diagram of the process of obtaining the patterned structures in the PMT composites. In this process, the sonicated solution containing both PVK and MWCNT was carefully cast on a glass Petri dish containing small circular discs with a diameter of 1 cm in the environment of 20 ℃ and relative humidity of 60 ± 2 %. Humid air was applied on the solution surface at its flow rate of 0.5 L/min. After complete evaporation of solvent, a ordered porous polymer film was obtained.

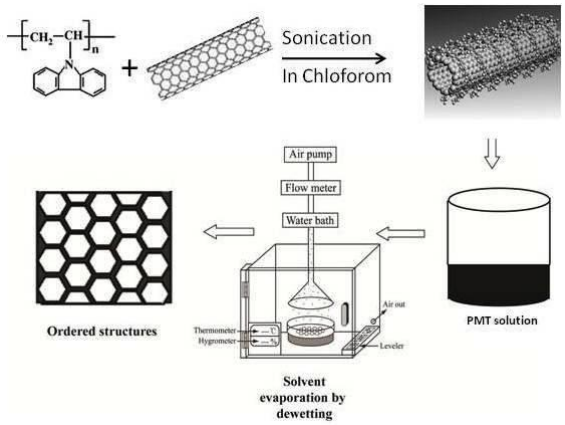

Fig.1. Schematic diagram showing the formation of the ordered structures through the dispersion of MWCNT in the PVK solution

3. Results and Discussion

3.1. Dispersion of MWCNT into polymer composite

If functionalized appropriately, MWCNTs can be dispersed in polymer solution [1,3].

In chemical functionalization, functional groups are covalently linked to the surface of CNTs, making their mechanical and electrical properties change a lot, as compared with pristine CNTs. On the contrary, non-covalent functionalization retains the structural integrity of CNTs and their properties are hence not disrupted, which is important for the following applications [3].

The observations have shown that a homogeneous dispersion of MWCNTs in the solution has achieved that without any chemical modification of MWCNTs.

3.2 Honeycomb patterns in the PVK and PMT composite films

Fig.2(a)–2(d) show the SEM images of the honeycomb patterned film obtained by PMT-1, PMT-5, PMT-10, and PMT-15 polymer composites at 20 μm magnification, respectively, at room temperature. The patterned structure of PMT-1 and PMT-5 was circular in nature, with an almost uniform pore size as shown in Figs. 2(a) and 2(b). However, the pore size of the PMT-5 film was smaller a little than that of the PMT-1 film. Observing the ordered structures of the PMT-5 film more closely, we can see that the pores with a different diameter are coexisting. Similar ordered structures were obtained in PVK-10 film and PMT-15 film as shown in Figs. 2(c) and 2(d); however, their pore-sizes were larger than those of PMT-5 film. The pore diameter of the ordered structures increased with an increase in MWCNT concentration in PMT-5, PMT-10, and PMT-15. The wall thickness between pores increased in the composite films where high amounts of MWCNTs were added (Figs. 2(b), (c) and (d)). This indicates that the ordered pattern in the composites films is mainly organized by the composition of PVK in the composites. Then, this result means that patterned films can also be fabricated by similar composite systems obtained by the dispersion of other inorganic materials into the PVK solution, which acts as an organizing backbone for the patterned films. DC conductivity of the patterned films was increased by increasing the concentration of MWCNTs in the composites.

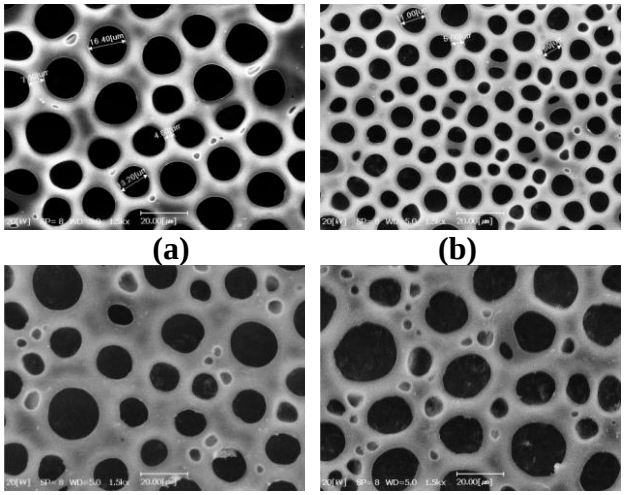

Fig. 2. Typical patterns investigated by SEM in the PVK-MWCNT composite films under the physical conditions of 20 ºC and a relative humidity of 60% with an air flow rate of 0.5 mL/min (a) for PMT-1, (b) for PMT-5, (c) for PMT-10, and (d) for PMT-15

4. Conclusion

We synthesized Poly-(*N*-vinylcarbazole) from NVK monomer and $FeCl_3$ used as an oxidizing agent. PVK was used in combination with MWCNT to preparation polymer composite material that was used to fabrication the well ordered film. The inclusion of MWCNT in PVK for the formation of PVK-MWCNT composites not only increased thermal stability but also increased the conductivity of PVK. This material can be a good candidate for some applications such as organic solar cells, optics and electronics device.

5. References

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