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Carbon nanotubes stabilize poly(vinyl chloride) against thermal degradation

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ABSTRACT

In this study, multiwalled carbon nanotubes (CNT), ball-milled CNT (bmCNT), and acid-treated CNT (CNT-COOH) were assessed as thermal stabilizers in poly(vinyl chloride) (PVC). Films of pure PVC, CNT/PVC, bmCNT/PVC, and CNT-COOH/PVC cast from tetrahydrofuran were subjected to thermal aging in N_2 in a test tube submerged in an oil bath maintained at 180 °C for a certain time. FTIR and UV-Vis spectra and discoloration of aged PVC composites were investigated on the formation of conjugated polyene structure in PVC. The results found that all three types of CNT of small amounts (0.1 or 0.3 phr) could stabilize PVC against thermal degradation by retarding the rate of formation of a conjugated polyene structure, with the stabilizing efficacy in the order of bmCNT > CNT > CNT-COOH. Moreover, Congo red and dehydrochlorination (pH measurement) tests were investigated on the degradation of PVC to HCl during the thermal aging as a function of time, CNT type and content. Thermal degradations of PVC to HCl were promoted by all three types of CNT in the initial 30 min of aging but were clearly stabilized against degradation over prolonged aging (for instance, 120 min) by bmCNT followed by CNT-COOH, both exhibiting the optimal stabilizing efficacy at 1 phr. The bmCNT was the most effective thermal stabilizer among the three types of nanotubes studied in PVC to resist both its discoloration and degradation of HCl. This newly-developed PVC composite with CNT as an additive provides an efficient route towards the development of highly thermal-stabilized PVC.

1. Introduction

Over the last fifty years, thermoplastic polymers have gained much attention in industry due to their excellent processability at high temperature, and unique elasticity and mechanical properties at room temperature that are suitable for various applications including manufacturing, biomedical, electronic and food packaging applications. Among the many types of thermoplastic polymers, poly(vinyl chloride) (PVC) is one of the most versatile materials due to its wide chemical resistance, excellent barrier properties and highly competitive price [1–3]. However, PVC is highly sensitive to ultraviolet (UV) light and elevated temperatures, and its polymeric structure deteriorates significantly when exposed to long-term elevated temperatures and UV [4–7]. Another major disadvantage in the manufacture and use of PVC is its low thermal stability. PVC tends to split off hydrogen chloride (HCl) at elevated temperatures, which in turn accelerates degradation of PVC, leading to the formation of conjugated polyene sequences of double bonds along the polymer chain and discoloration of the polymer [8–11]. Therefore, additives are frequently required to impart stability against the degradative effects of heat and UV and enhance the product quality and performance of PVC [12,13]. A number of approaches have been developed to improve the thermal stability and mechanical properties of PVC, such as physical blending [14,15], chemical copolymerization [16,17] and incorporation of different types of fillers such as wood flour [18], wood fibers [19], cellulose whiskers [20], calcium carbonate [21], two-dimensional layered clays [22,23] and carbon materials [24,25] into the PVC matrix as representative methods. Exfoliation of clay and graphite into the PVC matrix have recently attracted significant research

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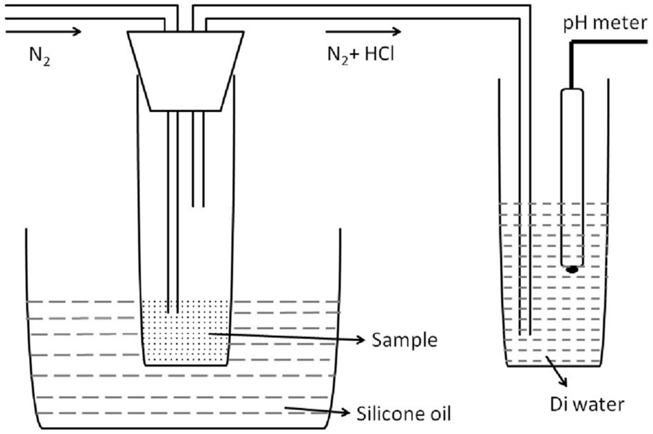

Fig. 1. Illustration of the thermal aging apparatus and connected HCl absorption tube used to assess thermal aging of PVC films and composites heated at 180 °C under N_2.

interests as exfoliation approaches are a more efficient route for fabrication of highly thermal stable PVC nanocomposites in comparison with existing methods for reinforced PVC composites. Although exfoliation of clay and graphite provides a convenient route to overcome the thermal stability limitations of PVC, complete dispersion and exfoliation of these two dimensional nanomaterials in the PVC matrix remains a formidable challenge.

In order to overcome the obstacles described above, surface treatment of carbon materials has received much interest as an efficient chemical functionalization method for dispersing carbon materials in solution [26,27]. Surface-functionalized carbon nanotubes (CNTs) are a common, one-dimensional carbon material that can be well-dispersed in the solution phase [28]. In recent decades, the fascinating physical and chemical properties of functionalized CNTs, such as their structural stability, electronic and mechanical properties, have attracted considerable attention and shown enormous potential for electronic and biomedical applications [29–32]. Recently, functionalized CNTs have been widely used as multi-functional fillers to produce CNT-polymer nanocomposites by melt blending [33,34], dispersal and casting [35,36], in situ polymerization [37,38], electrospinning [39,40], and extrusion [41,42] among other methods. These approaches effectively improve the electrical conductivity, and mechanical and thermal properties of the resulting nanocomposites [43]. Therefore, production of a homogeneous dispersion of CNTs in a polymer matrix has been an important area of academic research and industrial innovation in recent years. Some studies have demonstrated the addition of CNTs to a polymer matrix can reduce free radical formation and increase free radical scavenging, which provides an effective strategy to prevent or minimize the side effects of chemical reactions within polymers under gamma-ray irradiation in the presence of oxygen [44,45]. Thus, we hypothesized that incorporation of CNTs into the PVC matrix may provide an effective method to create a stable reinforcing phase within the polymer matrix and facilitate direct manipulation of the structural stability of PVC to enhance its long-term thermal stability and mechanical performance. Indeed, CNT-reinforced PVC composites constructed from surface-functionalized CNTs may enable the creation of various extents of CNT dispersion within a PVC matrix to achieve the desired performance and reliability for varied practical commercial and industrial applications.

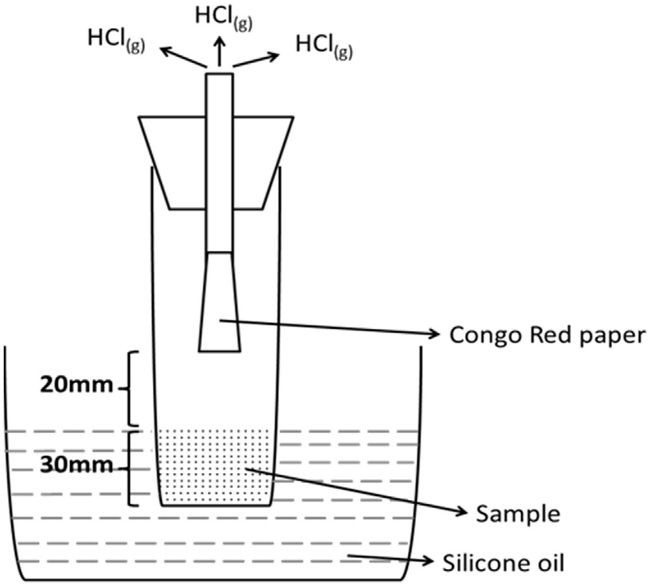

Fig. 2. Illustration of the Congo red test apparatus for assessing thermal stability of PVC and composite film samples heated at 180 °C. After a 10 min N_2 purge to completely remove air, the tube was immersed 30 mm into the silicone oil bath and the time taken for the Congo red test paper to change in color from red to blue was recorded.

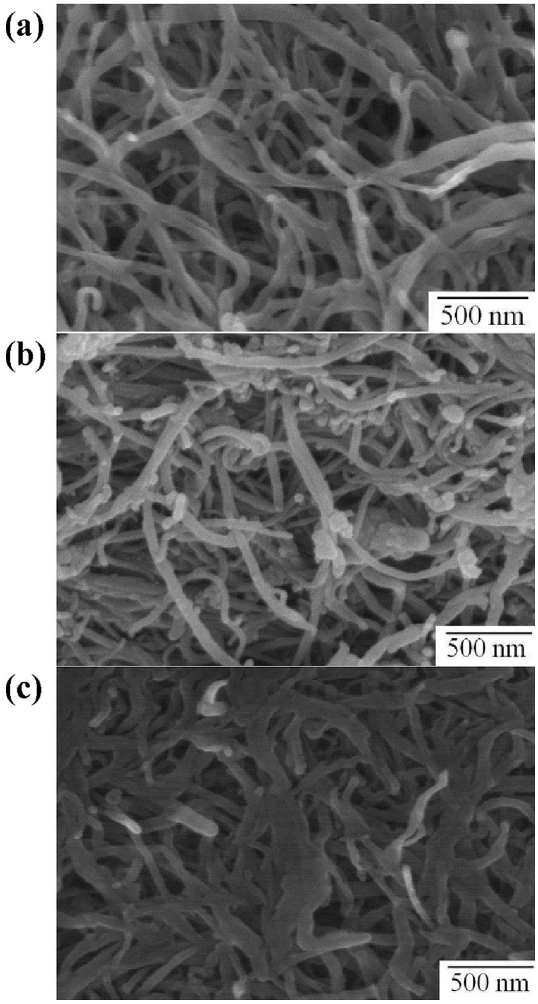

Fig. 3. FESEM images of (a) CNT, (b) bmCNT, and (c) CNT-COOH.