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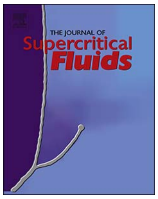

Poly(methyl methacrylate)-vapor growth carbon fiber-graphene nanocomposites prepared using supercritical CO_2 mixing and drying

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ABSTRACT

Supercritical carbon dioxide ($scCO_2$) has been employed in conjunction with vapor growth carbon fibers (VGCFs) and graphene nanoplatelets (GNPs) to enhance the properties (electrical, thermal, physical) of a poly (methyl methacrylate) (PMMA) matrix. When the VGCF loading was 10 wt.%, the electrical conductivity (9.33 S/m) of the PMMA-VGCF nanocomposite prepared through $scCO_2$ mixing at 103.4 bar and 40 °C was 15.6% greater than that obtained when using traditional mixing in *N*-methyl-2-pyrollidone (NMP). A synergetic effect existed for the VGCFs and GNPs, with the thermal conductivity of the PMMA-VGCF-GNP nanocomposite [0.492 W/(m K)] being 20.2% greater than that of the individual PMMA-VGCF nanocomposite [0.409 W/(m K)], after applying $scCO_2$ mixing. The advantages of the proposed $scCO_2$ technology are twofold: it enhances the dispersion of VGCFs and GNPs in the PMMA matrix and eliminates residual NMP after $scCO_2$ drying.

1. Introduction

Poly(methyl methacrylate) (PMMA), one of the most important industrial thermoplastic polymers, possesses excellent weatherability, good transparency, and high impact resistant. Therefore, PMMA materials have been applied extensively for household, military, and industrial purposes. The low electrical and thermal conductivities of PMMA materials, due to the amorphous and non-crystalline nature of the polymer, however, restrict their applications. Because traditional PMMA materials cannot always meet current market demands, reinforcing them has become common in the composites industry. Dispersing fillers into PMMA matrices can often improve their conductivity [1–5]. Furthermore, many methods have been used to improve the dispersibility and compatibility between fillers and the PMMA matrices.

First, direct melting blending is a common method for obtaining thermoplastic nanocomposites, particularly when employing a twin-screw extruder. This non-solvent method involves mixing a molten blend of the filler and the polymer matrix. The polymer chains intercalate or exfoliate to form nanocomposites at high temperature, the result of shear forces. PMMA matrices containing multi-walled carbon nanotubes (MWCNTs), graphene oxide (GO), or modified carbon nanotubes (CNTs) [*e.g.*, carboxylic acid-functionalized (CNTCOOH), polyethylene-modified (CNTPE)] – namely PMMA-MWCNTs, PMMA-GO, PMMA-base washed GO, poly[(α-methylstyrene)-*co*-(acrylonitrile)] (PαMSAN)-PMMA-CNTCOOH, or PαMSAN-PMMA-CNTPE – have been prepared using a twin-screw extruder [6–9]. Several risks should be taken into consideration when adopting this method: polymer degradation may be a significant issue during high-temperature operation, compatiblizers may also thermally degrade, and the fillers might readily aggregate – all of which might significantly worsen the mechanical properties of the final nanocomposite [10].

The second approach is *in situ* polymerization, where swelling of the filler within the monomer occurs prior to polymerization initiated by a heat source after diffusion of a suitable initiator. *In situ* polymerization is a direct and simple means of dispersing fillers into liquid monomers or precursors. This approach prevents agglomeration of the filler in the polymer matrix and improves the interfacial properties between the two phases. It has been used to synthesize nanocomposites from a variety of thermoplastic and thermosetting polymers. GO as a filler was used to synthesize PMMA-GO composites through *in situ* polymerization; the composites displayed enhanced storage tensile moduli and glass transition temperatures (T_g) [11]. MWCNTs at several concentrations have also been dispersed into methyl methacrylate (MMA) prior to *in situ* polymerization, thereby increasing the volumetric electrical conductivity of the composite by several orders of magnitude over that of PMMA [12–15]. In addition, supercritical carbon dioxide ($scCO_2$) has been used as a solvent to homogeneously distribute MMA for polymerization, allowing modified layered silicates to intercalate into the resulting PMMA matrix [16].

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Third, solution blending is a simple and relatively cheap method displaying high efficiency and operability. Several organic solvents [*e.g.*, methanol, tetrahydrofuran (THF), dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), and chloroform] can be used to dissolve the PMMA matrix, thereby decreasing its viscosity, allowing the filler to disperse or intercalate into it uniformly and readily [17–22]. The main difficulty with this method is ensuring that the fillers are dispersed effectively in the polymer matrix, because they are likely to aggregate under the conditions. Unfortunately, the latter two methods often need large amounts of appropriate solvents for the monomer and the polymer, leading to several environmental and cost issues. Residual organic solvents in the composite require removal through low-temperature post-processing, thereby extending the length of the processing period. Any resulting aggregation or agglomeration of the fillers would decrease the surface area as well as the volumetric reactivity, and make it harder to remove any remaining solvent. The presence of residual organic solvent or aggregated nanocarbon fillers (NCFs) also shortens the lifetime of a composite [7].

$scCO_2$ has been used in polymer processing to cause and improve foaming, swelling, the permeation of additives, and for extracting residues. Absorption of $scCO_2$ weakens the entanglement of polymer chains. This increases the free volume of the polymer and decreases its viscosity, glass transition temperature, and surface tension. Furthermore, $scCO_2$ has been used in the synthesis of several polymer-nanofiller composites [23]. PMMA-nanofiller composites have been prepared using direct blending, *in situ* polymerization, or solution blending. In this study, we used pristine vapor growth carbon fibers (VGCFs) and graphene nanoplatelets (GNPs) as NCFs. We prepared VGCF and GNP nanocomposites using $scCO_2$ mixing and traditional NMP mixing, and examined their dispersion, in addition to electrical, thermal, and physical properties. In addition, the residual NMP in the nanocomposites was removed when using $scCO_2$ drying, more so than in those obtained using subcritical CO_2 drying or vacuum drying.

2. Experimental

2.1. Materials

VGCFs (diameter: 100 nm; length: 3 μm; specific surface area: 17 m^2/g; graphitization degree: 90%) were purchased from Yonyu Applied Technology Material (Taiwan). GNPs (purity: 98.8%; specific surface area: 700 m^2/g; lateral size: 2 μm; average flake thickness: 4 nm) were synthesized from natural graphite powder according to the modified Hummer method [24]. The specific surface area of the GNPs was 40 times greater than that of the VGCFs, suggesting that the former possessed better dispersibility. PMMA having an average molecular weight (M_w) of 120,000 g/mol (GPC) and a density of 1.18 g/cm^3 was purchased from Sigma–Aldrich (USA). Transmission electron microscopy (TEM) images of the VGCFs featured black spots that indicated the presence of catalyst [Fig. 1(a)]. TEM images of the GNPs [Fig. 1(b)] revealed a semitransparent structure for the few-layer graphite flakes. NMP (99.9%) was purchased from Sigma–Aldrich (USA); carbon dioxide (99.5%) from Linde LienHwa (Taiwan).

Fig. 2 displays the Raman spectra of the VGCFs and GNPs; their I_D/I_G ratios were 0.069 and 0.827, respectively. In these Raman spectra, D bands (representing disordered structures or defects) appeared in the range 1250–1450 cm^{-1}; they reflect a breathing mode of rings of sp^2-hybridized carbon atoms and, if active, they must be positioned next to the edges or defects of the VGCFs or GNPs. For sp^2-hybridized carbon materials, G bands in the range 1500–1650 cm^{-1} result from C—C bond stretching that is sensitive to strain. The Raman spectra of the GNPs each featured a strong signal located at 2500–2800 cm^{-1}; this so-called 2D band for graphitic sp^2-hybridized materials represents a second-order two-phonon event that depends on the frequency of exciting laser light. The 2D band in the Raman spectra of the GNPs was more intense than that of the VGCFs; thus, these GNPs were highly crystalline in addition to having greater thermal conductivity and mechanical properties. The I_D/I_G ratio of the GNPs (0.827) was, however, 11 times greater than that of the VGCFs (0.069) because of the higher-intensity D band of the GNPs that resulted from the chemical exfoliation method.

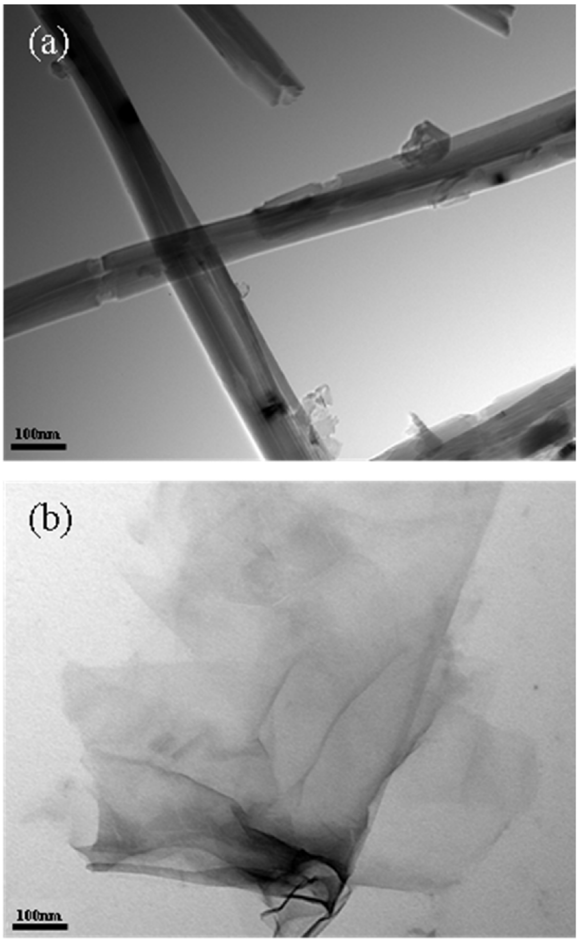

Fig. 1. TEM images of (a) vapor growth carbon fibers (VGCFs) and (b) graphene nanoplatelets (GNPs).

2.2. PMMA-VGCF-GNP nanocomposites

2.2.1. NMP mixing

NMP is commonly employed as a solvent for dispersing fillers into PMMA matrices [18,19]. Accordingly, we also employed NMP for the dissolution of solid PMMA with stirring, following by heating at 60 °C for various periods of time. A transparent PMMA-NMP solution of 25 wt.% was obtained without any solid particulates. VGCFs and GNPs were then added as NCFs to the solution, which was then subjected to ultrasonication for 2 h. The mixture was prepared with stirring at 300 revs per minute (rpm) at a temperature of 40 °C for 2 h. After the mixture had been placed in a vacuum oven to eliminate air bubbles, it was subjected to the solution-casting method. The nanocomposite was obtained after vacuum drying (1.33×10^{-3} bar, 40 °C, 1 h) to remove NMP. Herein, the resulting nanocomposite is denoted as “NMP nanocomposite”.

2.2.2. $scCO_2$ mixing

Fig. 3 shows the experimental apparatus used for $scCO_2$ mixing and CO_2 drying. The mixture was loaded into a glass bottle (50 mL) and placed in a high-pressure vessel. The vessel was equipped with a magnetic drive (Parr A1120HC) to provide trouble-free linkage to the internal stirrer (*i.e.*, anchor-type blade) which was able to mechanically agitate the NCFs and PMMA matrix. Residual air was removed from the