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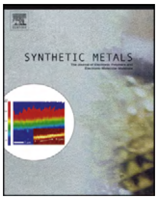

Fabrication and percolation behaviour of novel porous conductive polyblends of polyaniline and poly(methyl methacrylate)

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ABSTRACT

The conductive polymer polyaniline is blended with conventional industrial thermoplastics in order to obtain an electrically conductive polymer blend with adequate mechanical properties. Processing these polyblends into foams yields a porous conductive material that exhibits immense application potential such as dynamic separation media and low-density electrostatic discharge protection. In the current study, the morphology of a thermally processable blend consisting of an electrically conductive polyaniline-dodecylbenzene sulfonic acid complex and poly(methyl methacrylate) is explored using a two-phase batch foaming setup. The effect of blend composition and processing parameters on the resulting porous morphology is investigated. The impact of the underlying microstructure and blend composition on the frequency dependent electrical conductivity is elucidated using multiple linear regression and a model is proposed. Finally, dielectric analysis is utilized to experimentally identify the critical dispersion frequency of an unfoamed blend composition near the percolation threshold.

1. Introduction

Polymeric foams are porous materials whose inherent low densities are ideally suited for a wide variety of applications ranging from impact dissipating automotive parts, to mass-critical aerospace components, and acoustic and thermal insulation [1,2]. Porous structures are categorized according to their morphologies and one category of particular interest due to an attractive balance of mechanical properties is known as the microcellular foams [3]. These foams have average pore diameters on the order of 10 μm and pore densities on the order of 10^9–10^{15} pores/cm^3 [4].

Recent studies in the field of conductive polymers have identified a variety of scenarios for which porous conductive polymers would be advantageous to achieve improved ion migration rates and low-density conductive blends for electrostatic discharge protection and electromagnetic interference shielding [5–9].

This study serves to bridge the polymeric foam and conductive polymer technologies by means of the thermal doping of conductive polyaniline (PAni) with dodecylbenzene sulfonic acid (DBSA) in conventional thermoplastic parent phase to produce a novel porous conductive material with low-density properties realized through a two-phase batch foaming process. It is well-established that microcellular morphologies are readily obtained by the batch foam processing of poly(methyl methacrylate) (PMMA) [10–12], and that blends of PMMA and PAni-DBSA are miscible [13], thus PMMA has been selected as the parent phase of the polymer blends prepared in this study.

Unlike several previous studies of nonporous solution-processed polyblends of PAni-PMMA [14–16], the PAni constituent will be mechanically dispersed and thermally fused within the parent phase. The effect of blend composition, processing, and system parameters on the physical properties of the resulting porous structure are investigated with an emphasis on extending our previous work by fabricating a wide range of blend compositions in order to identify the effective percolation threshold range [17,18]. Finally, the impact of the microstructure on the frequency dependent electrical conductivity is elucidated.

2. Batch foaming process

The batch foaming process exploits the pressure dependent solubility of gasses in polymer systems. Four major phenomena govern the batch foaming process: formation of a gas-polymer solution, pore nucleation, pore growth, and morphology stabilization [19]. As illustrated in Fig. 1(a), the multiphase solution is obtained by subjecting the specimen to an inert atmosphere at elevated pressure for a certain duration such that the the solubility limit is reached [20,21].

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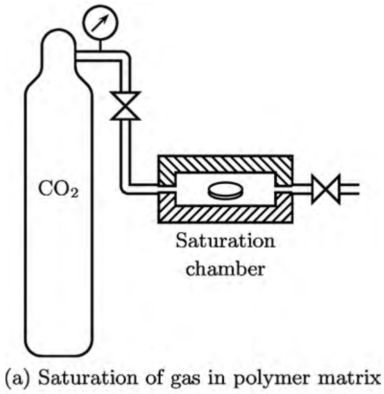
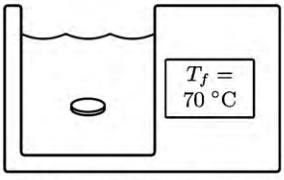


(a) Saturation of gas in polymer matrix



(b) Pore nucleation and growth

Fig. 1. A schematic representation of the two-phase batch foaming process.

For a given gas-polymer system, the saturation time is proportional to the square of the specimen thickness according to

$$t_{\text{sat}} = \frac{\pi h^2}{16D}, \tag{1}$$

where t_{sat} is the saturation time, h is the specimen thickness, and D is the diffusion coefficient [22]. Hence, a disc geometry of the specimen has been stipulated such that the aspect ratio of the specimen results in a small height, thereby minimizing the required saturation time. Such a configuration is also conducive to accurate dielectric analysis.

Once saturated, pore nucleation is induced by a rapid pressure drop from opening the exhaust valve of the chamber [23]. The decline in pressure results in a reduction in the solubility of the gas within the polymer phase, and gas molecules cluster and form pore nuclei.

The temperature of the specimen is then raised to reduce the stiffness of the polymer phase, thereby further promoting the pore growth process. As indicated in Fig. 1(b), this increase in temperature is realized by immersing the specimen in a hot water bath. The degree of pore growth is proportional to the duration of the immersion, which is referred to as the foaming time, t_f.

Pore stabilization is achieved by quenching the specimen in cold water, thereby simultaneously re-establishing thermodynamic stability and raising the stiffness of the polymer phase, which in turn arrests successive pore growth.

3. Experimental methodology

3.1. Blended sample preparation

The PMMA (Sigma–Aldrich, $M_w \approx 120{,}000$) and PAni emeraldine base (Sigma–Aldrich, $M_w \approx 300{,}000$) powders were initially dried under a −15 in. Hg vacuum at 60 °C for a minimum of 3 d to reduce the moisture content of the powder.

To overcome the typical restrictions associated with the infusible and insoluble nature of the conductive emeraldine salt form of PAni, a thermally processable conductive complex of PAni was prepared without the requirement for auxiliary solvents using DBSA (Sigma–Aldrich) as the dopant [24,25]. The PAni-DBSA complex was formed by mixing the components in the optimal 1:3 mass ratio until a paste formed. The paste was then thermally processed in a twin-screw compounder (MiniLab II HAAKE Rheomex CTW5, Thermo Fisher Scientific) operating at 140 °C. The screw speed was maintained at 20 rpm to provide sufficient residence time for the characteristic paste-to-solid transition to take place, however the recirculation was not utilized to avoid the detrimental aging effects associated with prolonged exposure to elevated temperatures [26]. The resulting product was then cryogenically ground into a fine powder to improve dispersion within the PMMA parent phase.

Various compositions of the PAni-PMMA mixture were then prepared by compounding premixed ratios of the powders at 180 °C and 50 rpm. The resulting product is then deposited within a 1.75 mm thick die consisting of 12 through-holes approximately 20.0 mm in diameter.

The die is then placed between the heated plates of a hydraulic press at 180 °C under 3.9 MPa of pressure for 3–4 min [3]. The die is then removed from the press and quenched in water to facilitate the removal of the specimens from the die. Finally, the samples are dried at ambient conditions for a minimum of 18 h before characterization. Once completely dry, the specimens are referred to as being in the *unfoamed* condition. In the present investigation PAni-PMMA blends of $\phi = 0$ (pure PMMA), 0.01, 0.02, 0.05, 0.10, 0.20, 0.35, 0.50, and 1.00 PAni-DBSA were prepared, where ϕ denotes the mass fraction of PAni-DBSA in PMMA (note that due to the similar density of the blend constituents, the volume fraction of the conductive filler is approximately equal to the mass fraction). In this regard, the composition specifications denote the ratio of PAni-DBSA to PMMA, the actual PAni content nominally being a fraction of the total PAni-DBSA content.

3.2. Microcellular processing

Compressed carbon dioxide at a pressure of 810 psi (5.6 MPa) was utilized as the gas blowing agent, and specimens were saturated for 18 h, after which they were considered fully saturated [27]. A water bath having a temperature of 70 °C was utilized to facilitate cell growth, and specimens of varying composition were characterized in the unfoamed condition, foamed condition with $t_f = 5$ s, and foamed condition with $t_f = 15$ s.

Once foamed, the specimens were quenched in cold water to arrest the cell growth, and subsequently dried to minimize the effects of moisture content and residual CO_2 on the foamed condition characterization process. Previous work has shown that the saturation and subsequent desaturation of the composite with CO_2 does not have a significant impact on the electrical conductivity of the material [28].

3.3. Characterization of porous morphology

Characterization of the specimens was performed via the measurement of several physical parameters. Physical data collection consisted of the determination of the characteristic dimensions and mass of each sample using a vernier caliper and precision balance respectively. An approximated volume and the corresponding mass measurement were then used to estimate the density of the specimen. This characterization procedure was performed on each sample in both the unfoamed and foamed condition such that the relative density, ρ, was determined. The relative density is indicative of the degree of volume expansion and is given by

$$\rho = \frac{\rho_f}{\rho_p}, \tag{2}$$

where ρ_f and ρ_p denote the density of the specimen in the foamed and unfoamed (polymer) state respectively. Relative density mea-