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3D porous polymeric conductive material prepared using LbL deposition

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ABSTRACT

In this work a 3D porous polymeric conducting material is derived from a multi-percolated polymer blend system. The work has focused on the preparation of low surface area porous substrates from polymer blends followed by the deposition of polyaniline conductive polymer (PANI) on the internal porous surface using a layer-by-layer (LbL) technique. The approach reported here allows for the percolation threshold concentration of polyaniline conductive polymer (PANI) to be reduced to values of no more than 0.19%. Furthermore, depending on the amount of PANI deposited, the conductivity of the porous substrate can be controlled from 10^{-15} S cm^{-1} to 10^{-3} S cm^{-1}.

Ternary and quaternary multi-percolated systems comprised of high-density polyethylene (HDPE), polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF) are prepared by melt mixing and subsequently annealed in order to obtain large interconnected phases. Selective extraction of PS, PMMA and PVDF result in a fully interconnected porous HDPE substrate of ultra-low surface area and highly uniform sized channels. This provides an ideal substrate for subsequent polyaniline (PANI) addition. Using a layer-by-layer (LbL) approach, alternating poly(styrene sulfonate) (PSS)/PANI layers are deposited on the internal surface of the 3-dimensional porous polymer substrate. The PANI and sodium poly(styrene sulfonate) (PSS) both adopt an inter-diffused network conformation on the surface. The sequential deposition of PSS and PANI has been studied in detail and the mass deposition profile demonstrates oscillatory behavior following a zigzag-type pattern. The presence of salt in the deposition solution results in a more uniform deposition and more thickly deposited PSS/PANI layers. The conductivity of these samples was measured and the conductivity can be controlled from 10^{-15} S cm^{-1} to 10^{-5} S cm^{-1} depending on the number of deposited layers. In the case of a porous sample which can be crushed, applying a load to the substrate can be used as an additional control parameter. In that sample a high load results in higher conductivity with values as high as 10^{-3} S cm^{-1} obtained. The work described above has focused on very low surface area porous substrates in order to generate a conductive device with the lowest possible concentration values of polyaniline, but high surface area substrates can also be readily prepared using this approach.

1. Introduction

One of the main contributions in polymer physics over the last 20 years has been the development of electronic devices consisting of conducting polymers [1–7]. This work has led to: the thin film deposition and microstructuring of conducting materials [1]; materials for energy technologies [2]; electroluminescent and electrochromic devices [3]; membranes and ion exchangers [4]; corrosion protection [5]; sensors [6] and artificial muscles [7]. Electron conductive polymers, which are the result of extended π-conjugation along the polymer backbone, fall into the class of conductive materials exhibiting semi-conducting behavior. The discovery of polymer light emitting diodes [8], in particular, has brought considerable attention to the efficacy and lifetime of semi-conducting polymer-based electronic devices. The magnitude of the electrical resistivity, or conductivity, determines the application field of the device and these polymeric optoelectronic devices can be classified in a number of different categories including: antistatic applications with a range of 10^{-14}–10^{-9} S cm^{-1}; electrostatic dissipation applications with a range of 10^{-9}–10^{-5} S cm^{-1}; and semi-conducting applications with a range of 10^{-6}–10^{0} S cm^{-1} [9]. By controlling the range of the conductivity, the development of devices such as polymeric photovoltaic devices [10], polymer-based lasers [11], and transistors [12] has received considerable attention recently.

Some of the principal approaches used in the preparation of polymeric conductive devices are the fabrication of ultrathin films by various strategies such as the Langmuir–Blodgett (LB) technique [13] and the self-assembled monolayer (SAM) method [14]. As well,

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layer-by-layer (LbL) assembly allows for a high degree of control of material properties and architecture at the nanometer scale [15,16]. In less than 20 years since the introduction of the LbL technique [17], the electrochemical study of LbL films has grown from theory to functional devices, but, in most cases, thin films of conductive polymer are applied on 2D surfaces. One of the main requirements in this field is to further expand the range and potential of 3D conductive polymeric devices.

In an A/B heterophasic polymer blend, a low concentration of phase A forms droplets in a matrix of phase B. As the concentration is gradually increased the percolation point is reached and the continuity of phase A also increases. Near the phase inversion region a co-continuous morphology is observed [18]. A co-continuous morphology is defined as a state where each phase is completely continuous throughout the material. The co-continuous phase structure consists of two fully interconnected phases which mutually interpenetrate each other [19]. The percolation threshold is defined as the formation of long-range connectivity in random systems. Solid droplets typically demonstrate a percolation threshold at values of 0.16 by assuming that the occupation of a site or bond is completely random. A topic of significant interest in heterophasic polymer blends has been to examine the various factors which results in significant reductions in the percolation threshold concentration [20,21]. One of the most interesting approaches towards low percolation thresholds is the development of double percolated structures [22,23]. Zhang et al. [24] reported on a thermodynamically driven double percolated morphology in an HDPE/PS/PMMA blend which was essentially a fully continuous system, PS, encapsulating an already continuous system, PMMA. This type of structure allowed the percolation threshold for the encapsulating polymer to be reduced to well below 3%. This work demonstrated the potential of layering one phase onto another continuous structure as a powerful technique to reducing percolation thresholds.

In a ternary liquid system complete wetting can be described when one phase tends to spontaneously spread on the second phase in the matrix of third phase. For this purpose, Torza and Mason [25] and then Hobbs et al. [26] employed modified Harkins spreading coefficients (λ_{ij}) which is a simple and useful mathematical expression and thermodynamic explanation to predict wetting characteristic (phase morphology) of ternary systems.

$$\lambda_{ij} = \gamma_{jk} - \gamma_{ik} - \gamma_{ij} \quad (1)$$

λ_{ij} is defined as the spreading coefficient giving the tendency of component (i) to encapsulate or spread onto component (j) in the matrix of component (k). It can also physically be defined as the transition between the non-wet and wet states. γ_{ij}, γ_{ik} and γ_{jk} are the interfacial tensions of the different polymer pairs. A positive value for the spreading coefficient, such as λ_{ij}, determines that phase (i) spreads over phase (j) while negative values for all possible spreading coefficients indicates separately dispersed phases in a continuous matrix.

In co-continuous polymer blends, the solvent extraction of one phase is a route towards porous materials with a fully interconnected porosity. A number of studies have shown that the phase size of co-continuous structures can be closely controlled from about 100 nm to hundreds of microns. The interfacial tension and an annealing step are critical parameters in this regard. One of the most important ways to coarsen, or increase, the phase size of a co-continuous network is melt annealing [27]. It has been shown that the annealing of a PS/PE system could increase the phase size from 0.9 to 72 μm [28]. Yuan et al. [27] observed a linear time dependence for the coarsening of immiscible co-continuous blends and proposed a capillary pressure effect as the driving force of the coarsening process during static annealing. In the static coarsening of co-continuous polymers, some very low level flow does occur since the systems are fully interconnected throughout the material. This is why the static coarsening of co-continuous systems is much more significant than that for dispersed phase systems. Clearly, highly controlled co-continuous morphologies can be converted into highly controlled porous materials through the selective extraction of one of the phases.

The layer-by-layer deposition technique to produce a polyelectrolyte multilayer on the surface of a flat substrate was proposed by Decher et al. [29]. In the LbL approach, the adsorption process involves consecutive and alternate deposition of positively and negatively charged polyelectrolytes driven by electrostatic forces followed by a rinsing step with water. A number of factors can influence mass deposition by LbL such as: ionic strength [30], pH of solution [31], molecular weight of polyelectrolyte [32], concentration of polyelectrolytes [33], and charge density [34]. Repetitive deposition steps provide a precise control over the total thickness of the layers in the range from a few angstroms up to a few micrometers. The thickness increment after each deposition is referred to as a growth rate which is dictated by polyelectrolyte geometry, surface charges, and solution parameters [35]. Some of the most widely used polyelectrolytes are sodium poly(styrene sulfonate), poly (diallyldimethyl-ammonium) chloride, poly(ethyleneimine), poly (allylamine), poly(vinyl sulfate), and poly(acrylic acid). Recent advances in LBL techniques, in the non-conductive area, have demonstrated the possibility of templating multilayers onto 3D scale substrates. Caruso et al. [36] deposited LBL films onto a colloidal core. Subsequent removal of the core resulted in a thin-film shell. Roy et al. [37] deposited LBL films onto a fully interconnected porous PLLA surface and the subsequent removal of PLLA resulted in a 3D object comprised of a vast nanosheath network of high surface area and the highest void volume ever reported for a polymeric substrate.

Rubner et al. [38,39] were the first to apply the LbL technique in the field of electronically conductive polymers to construct poly (styrene sulfonate) (PSS)/polyaniline (PANI) bilayers onto thin films in order to prepare a conductive device. Important advances have been made in this area by employing various conjugated polymers such as polyaniline and polypyrrole [40–42]. Ferreira et al. [43] found that the solubility of PANI in an organic media such as dimethylacetamide (DMA) is much higher than that in water. A solution of doped polyaniline generally makes it more difficult to achieve the spontaneous adsorption of polyaniline chains onto a variety hydrophilic and hydrophobic surfaces [38]. The presence of salt in the solutions has a subtle effect. Generally, it screens the monomer–monomer repulsive interactions, leading to enhancement of adsorption [44]. Salt can play different roles in polyelectrolyte multilayer (PEM) formation and function, such as controlling the thickness increment of polyelectrolytes, the permeability [45], and the stability [46] of the multilayer. Most of the work published so far has revealed an increase in conductivity with an increase in the number of adsorbed PSS/PANI bilayers by measurement of electrical conductivity of LbL films deposited on a flat surface [47,48]. In most cases conductivity measured by four-point probe increases continuously with addition of layers until a saturation plateau is reached around the 13th bilayer or 25th layer.

Several other methods of preparation of conductive polymers have also been reported [49–51]. The most well-known method is melt blending in which, through the control of morphology and confining the pathways of the conductive materials in a multiphase system, a high conductivity with low percolation threshold can be achieved [20,52]. In this case, percolation thresholds of 3wt% carbon black [20] and 20wt% PANI [52] for melt-blended samples were obtained. A variation on the blend theme for generating anisotropically conductive material is to use block copolymers in