Polymer Based Continuous Offset Printing

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ABSTRACT

Polymeric materials have tremendous potential for nano and micro-structured products because of their fabrication ease and wide property range. In contrast to other manufacturing approaches, fabrication processes for polymers are cost-effective and rapid. This work presents novel manufacturing approaches for the incorporation of nano/microscale functionality that are environmentally friendly (melt-based), industrially relevant, and can be transferred to a continuous offset printing based process. Nano or micro-structured surfaces with patterns of different polymers or nanoparticles can be made with directed assembly and transfer to a polymer substrate. The integration of template directed assembly of conducting polymers or nanoparticles into nanoscale patterns followed by transfer to a polymer substrate using a continous roll to roll process provides a method to prepare unique structures for flexible electronic devices, metamaterials, structural nanocomposites, icephobic surfaces or biocompatible materials. The work will present offset printing of conducting nanoelements, the fabrication of metamaterials for near-IR and microwave, and the effect of polymer type on the transfer efficiency. This process can be coupled with nanoscale embossing using our two-stage roll to roll line. Substrate materials can include designer nanocomposites (thermoplastic polymers with nanoclays, CNTs, silver nanoparticles, etc.) by integrating a roll-to-roll processes with continuous, melt based twin-screw extrusion.

Keywords: directed assembly, roll to roll, nanocomposites

1 INTRODUCTION

The transfer of nanoscience discoveries into commercial products would enable the development of lighter weight materials, smaller sensors, improved medical products, and smaller electronic devices. For fabrication of these devices novel manufacturing approaches are needed that are flexible, rapid, and easily integrated into industrially relevant manufacturing processes. Nanomanufacturing processes have emerged in many areas, such as polymer nanocomposites electronics [1], and biological systems. [2], Polymer materials are attractive for many applications because they can be processed with high rate fabrication methods at relatively low temperatures, are lightweight and can have a range of material properties. Processing methods include injection molding, compounding with fillers, extrusion processes and continuous roll to roll processing approaches. Thus, polymers can be easily adapted to many nanomanufacturing processes. These nanomanufacturing approaches include injection molding of nanoscale features, twin screw extrusion to form nanocomposites[3], and multi-layer films by extrusion[4],[5],[6]. For some applications there is a need to pattern two polymers (polymer blends) into controlled micro and nanoscale morphologies using directed assembly[7],[8],[9]. Directed assembly of nanoelements (e.g. conducting polymers[10], nanotubes[11]) followed by transfer to a polymer allows for preparation of unique structures, such as conducting polymers on an insulating polymer substrate for metamaterials or flexible electronics. A continuous process for directed assembly and transfer can be considered as a nanoscale offset printing process. Other nanomanufacturing processes can be used to prepare unique substrates for the offset printing process.

2 POLYMER OFFSET PRINTING

2.1 Printing of nanoscale structures

Nanopatterned polymers can be used for applications such as biosensors[12], and templates for nanolithography.[13] These applications often require nonuniform patterned polymer geometries, as may be needed in layouts for integrated circuits[14] or metamaterials. Polymer blends offer unique advantages for these applications, since blending two commercially available polymers offers a wide range of materials and may be cost efficient. Ease of patterning non-uniform geometries and fabrication of multiple length scale patterns on a single substrate (or operation) are additional advantages. The blends can be either patterned in a two step process, where the polymer is assembled first, followed by a transfer step to a secondary polymer substrate or a polymer blend solution can be patterned directly onto chemically functionalized substrates. Alternatively, a nanoelement, such as a conducting polymer , carbon nanotubes, or nanoparticles can be patterned and then transferred to a secondary polymer substrate. This method allows transfer to a wide range of thermoplastic polymer substrates.

In the two step process, a nanoelement, such as carbon nanotubes or conducting polymers, is patterned using

electric fields. A subsequent process is used to transfer the patterned nanoelement to a secondary substrate, in this case a flexible polymer. While solution casting can be used to transfer the patterned nanoelement, melt based processes, such as thermoforming are preferred and have been used to transfer both MWNTs[15] and a conducting polymer. In this method, the assembled CNTs on the template and heated polymer substrate come in contact using pressure and vacuum. A schematic of the printing process is shown below in Figure 1.

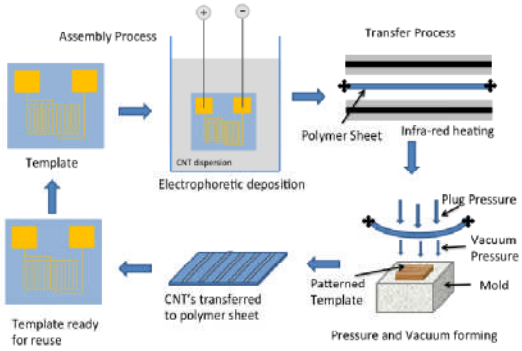

Figure 1: Schematic of the process cycle for assembly and transfer of MWCNTs by thermoforming.

Pulsed electrophoresis (pulses the electric current through the template in on and off cycles) can be used to increase template durabililty[16]. The duration of current on/off time in this study was 200 ms, and the ramp time up to 3V DC was 50 ms. Optimal deposition of PANi on the template occurred at 30 pulses. Research showed pulsed electrophoresis decreased the residual heat build-up in the template by more than 50 percent allowing for increased template lifetime with higher applied voltages. The process lends itself to a roll to roll or continuous offset printing process. In this process the nanoelements (here PANi is used) are assembled in a bath by pulsed electrophoresis, followed by transfer to a heated sheet. The polymer substrate was first heated by ceramic infrared heaters. For the transfer experiments the processing temperatures for PETG, TPU, PP, and PS were optimized based on the thermoforming process(Figure 2).

Figure 3 shows the results for transfer of PETG as a function of belt speed. For the PETG sheet, the transfer decreased with belt speed. Results with other polymers showed variation in transfer with the type of polymer sheet. More polar polymers showed better transfer of the PANi compared to non-polar polymers, but all materials showed reduced transfer with increased belt speed.

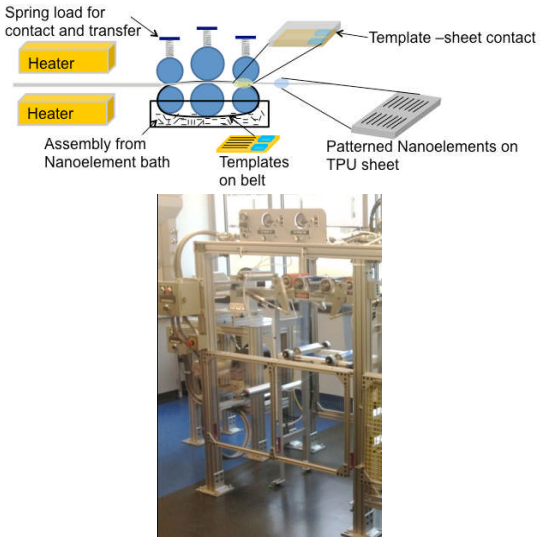

Figure 2: Experimental setup for roll to roll processing.

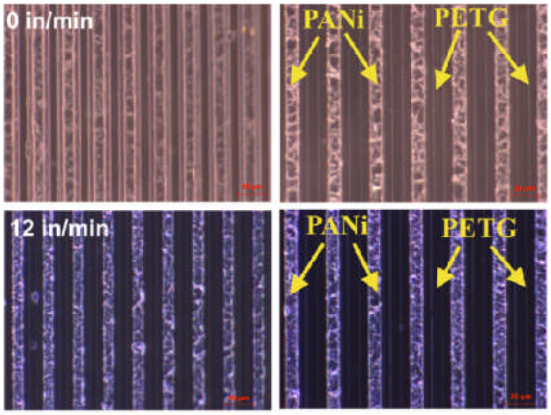

Figure 3: Optical micrographs showing the transfer of PANi on PETG surface at different belt speeds.

In the single step process, the two polymers are patterned directly from solution onto a surface that is chemically functionalized to attract each polymer to a specific location on the template surface. Assembly of polymer blends into both nonuniform and uniform patterns using chemically functionalized surfaces has been demonstrated[17],[18],[19],[9]. By this process it is also possible to deposit nonuniform patterns and multiple length scales on a single substrate (See Figure 4). Metrology for this process also consists of microscopy images after fabrication. In this case, metrology may be more challenging because of the use of two polymer materials.

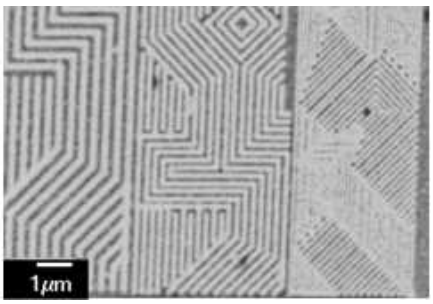

Figure 4: Polystyrene and polymethyl methacrylate patterned into nonuniform geometries and multiple length scales on a single template

The continuous offset printing process can be used to fabricate unique structures such as chiral metamaterials (Figure 5).


Figure 5:. Flexible chiral metamaterials.

2.2 SUBSTRATES

2.2.1 Nanocomposites

Polymers are often mixed with nanoscale fillers (polymer nanocomposites) to improve properties with low loadings. Numerous nanocomposite materials have been studied, including nanofillers such as nanoclay[20], carbon nanotubes[21], silica fillers, and other fillers mixed with both thermoset and thermoplastic polymers. Nanocomposites are made by mixing the polymer with the filler using: solution mixing, in-situ polymerization methods, and melt mixing. In-situ polymerization and solution methods provide good dispersion, but melt-mixing is advantageous because it does not use solvents and is more industrially compatible. Melt mixing uses mechanical and thermal energy to melt the polymer and disperse and distribute the filler into the polymer matrix. It has been used to fabricate a wide range of different nanocomposites using different fillers and polymers. Since nanofillers are typically agglomerated because of the strong interparticle interactions. The primary purpose of mixing is to break up the agglomerates to the primary particle through shear forces (dispersion). Property improvements are very dependent on the level of filler dispersion (final particle size), distribution (consistency of composition), and possible orientation (fibrous fillers). Thus, careful control of the mixing process, such as the industrially relevant melt mixing processes: twin screw extrusion or batch mixing, is critical. In the twin screw extrusion process, solid polymer and nanoparticles are fed into the twin screw extruder, the polymer is melted and the filler mixed into the melted polymer (Figure 6). The efficacy of mixing is controlled by process variables, such as screw speed, residence time, melt temperature, etc. Materials compounded by batch mixing and twin screw extrusion may be fabricated into a variety of shapes using typical plastics processing methods such as injection molding, extrusion, thermoforming, etc. Thus, nanocomposites can be used as designer substrates in an offset printing process providing unique material configurations.

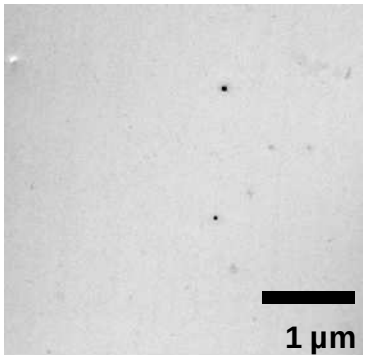

Figure 6: Example of well mixed nanosilver 0.1 wt% in polymer matrix.

2.2.2 Multi-layer Coextruded Films

The coextrusion process combines two extruded polymer melts to produce films with unique properties. This process has been used to prepare multilayer films for improved properties, including barrier and toughness[22],[23]. Films are produced by dividing the polymer melt into two streams and then stacking them on top of each other. With each splitting and stacking process repeated, the number of layers is increased[6]. While typically the multilayer films are prepared as horizontal layers, it is also possible to produce films with vertical layers. Vertical layers occur across the film and a single material spans the thickness of the film, while horizontal layers are stacked across the width of the film. Figure 7 shows a multi-layer film with horizontal layers. These multilayer films can include a layer with nanoparticles mixed using the processes described above.

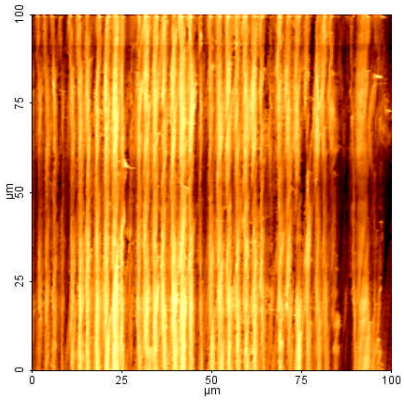

Figure 7: Horizontal nanolayered polymer film produced by multilayer co-extrusion.

3 CONCLUSIONS

Polymer materials are attractive for nanomanufacturing because of their ease of processing, light weight and flexibility. Frabrication of patterned polymer structures can be accomplished by nanoscale offset printing in a roll to roll process. This technique used the integration of high rate assembly of PANi by pulsed electrophoresis with the thermally assisted transfer in a roll-to-roll process. Substrates can be prepared from nanocomposites by continuous mixing, and multi-layer extrusion.

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