# Polymer Nanomanufacturing Strategies for Multifunctional Nanomaterials

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## ABSTRACT

Polymeric materials offer tremendous potential for preparing functional materials using nanoscale fillers and features. For example, the use of nanolayered materials in barrier or optical applications, nanofeatured materials for hydrophobic surfaces, and patterned polymer blends for biological and lithography applications. The utilization of these developments is hampered by the lack of methods to fabricate these structures in a reliable and cost effective manner. High rate, large area fabrication techniques using conventional and novel approaches to facilitate the commercialization of nanotechnology enabled products include; the directed assembly of nanoelements (conducting polymers, carbon nanotubes) followed by transfer to a polymer to fabricate unique nanopatterned structures, the directed assembly of polymer blends into nonuniform, multi-scale geometries, multi-layer materials by co-extrusion, and nanocomposites. .

***Keywords***: nanocomposites, nanomanufacturing, coextrusion, polymer blends, directed assembly.

## 1 INTRODUCTION

Nanotechnology offers potential for novel materials and functional devices with unprecedented performance, greater sensitivity, coupled with lighter weight. Polymeric materials are light weight, come in many forms, and can be processed using high rate manufacturing processes. Thus, polymers are an excellent platform for nanomanufacturing. They can be fabricated by numerous processes including extrusion, injection molding, compression molding, electrospinning, and compounded with nanoscale fillers. Polymer blends can be patterned into controlled micro and nanoscale morphologies by directed assembly. The directed assembly of nanoelements (e.g. conducting polymers) followed by transfer to a polymer can also be used to fabricate unique structures, such as flexible electronics. Each of these processes offers novel opportunities for fabrication of new materials and functionality. For example, the use of coextruded multilayer materials in barrier or optical applications, nanofeatured materials for hydrophobic surfaces, and the directed assembly of polymer blends into nonuniform, multi-scale geometries for biological and lithography applications. Moreover, several processes can be combined and integrated. The utilization of these developments is hampered by the lack of methods to fabricate these structures in a reliable and cost effective manner. High rate, large area fabrication techniques using conventional and novel approaches to facilitate the commercialization of nanotechnology enabled products are needed. The work presented here focuses on polymer based nanomanufacturing approaches, including coextrusion of multilayer films [1,2,3], electrospinning of nanofibers[4,5,6], nanocomposite fabrication [7], patterning of polymer blends [8,9,10] and directed assembly and transfer of nanoelements (nanotubes[11] and conducting polymers[12]).

## 2 POLYMER NANOMANUFACTURING

### 2.1 Melt Mixed Polymer Nanocomposites

Polymer materials are often combined with fillers to reduce cost or provide property enhancements. With the advent of new and novel nanofillers, research on the properties of mixtures of polymers with nanofillers (polymer nanocomposites) has steadily grown. The use of nanofillers in a polymer matrix was originally pioneered by the Toyota research group in the early 90's for polyamide-6/clay nanocomposites [13] In the years following, many other nanocomposite systems have been investigated. Nanofillers such as nanoclays [14], silica fillers, carbon nanotubes [15], and many others have been mixed with a wide array of thermoplastic and thermoset polymers.

While significant research activity has occurred for these polymer nanocomposites, applications have begun to emerge. Applications for polymer clay nanocomposites are the most broad and include automotive (e.g. the step assist component by GM), packaging (e.g.improved barrier materials for beverage containers[16]), and aerospace [17]. Carbon nanotube (CNT) reinforced polymers show improved toughness and are attractive for mechanical components. Polymer/CNT nanocomposites show improved electrical properties and are intriguing for EMI shielding applications.

Preparation methods for nanocomposites include solution mixing, in-situ polymerization methods, and melt mixing. Dispersion is typically higher for solution and in-situ polymerization approaches, but melt-mixing is more



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compatible with industrial processes and the lack of solvent is more environmentally friendly. Nanocomposites have been fabricated using melt mixing for a range of polymers, primarily with nanoclay fillers.

Melt processing of nanocomposites includes such techniques as batch mixing and extrusion. These processes impart mechanical and thermal energy to the mixture to fluidize the polymer and disperse and distribute the nanofiller into the polymer matrix. The nanofiller is typically agglomerated because of strong interparticle interactions, so that one of the purposes of mixing is to break apart the nanofiller into the primary particle through shear forces (dispersion). Surface modification to compatibilize the nanofiller in the polymer matrix is also used to help improve dispersion.

The property enhancements imparted to the nanocomposite depend on the filler dispersion (final particle size), distribution, and orientation (for high aspect ratio fillers). Since processing parameters control the final particle size, orientation and distribution, control of processing parameters is critical for optimizing property enhancements. For example, while high thermal energy will reduce the polymer viscosity, too high a temperature will degrade the polymer. Longer mixing times also improve the dispersion, however, excessive mixing can also result in degradation. Thus, to produce high quality polymer nanocomposites, good control of the mixing process is essential.

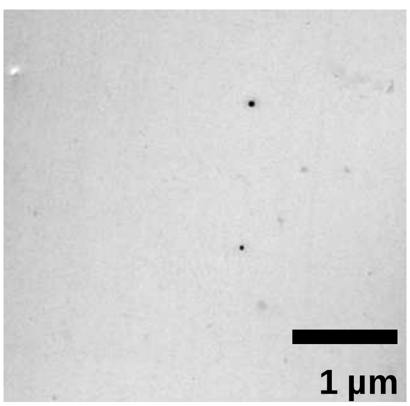



Figure 1: Nanosilver 0.1 wt% melt mixed.

In the work here, the fabrication of nanocomposites is done in industrially relevant processes, such as twin screw extrusion. In the twin screw extrusion process, nanoparticles and solid polymer pellets are fed into the twin screw extruder, where the polymer is melted and mixed with the filler (Figure 1). The resultant polymer nanocomposite melt is then fed through a die, forming a strand, which is cooled in a water bath and then pelletized. Materials compounded by the twin screw extrusion process can then be fabricated into a variety of shapes by injection molding, extrusion, thermoforming, etc. During compounding the degree of mixing is controlled by process variables, such as screw speed, residence time, melt temperature, etc. In general with better mixing, the greater the properties of the final nanocomposite. The effect of fill factor [18] and process parameters [19] on degree of mixing have been quantitatively [20] studied.. A range of different nanofillers and polymers have been mixed using this melt-based mixing method, such as nanoalumina, nanoclay, carbon nanotubes, graphene, fullerenes, and silica fillers.

## 2.2 Multi-layer Coextruded Films

Coextrusion has been used to produce multilayer films for improved properties, including barrier and toughness [21, 22]. These films are fabricated by dividing the melt into two streams, stacking these streams, and then recombining the two melt streams. With repeated splitting, stacking, and recombining process, the desired number of layers can be obtained as described by Ho et al. [23]. Typically the multilayer films are produced with horizontal layers, but vertical layers can also be produced. Horizontal layers occur through the thickness, while vertical layers occur across the width of the film. In each case, controlling instabilities is the major obstacle to fabrication.

Wave instabilities are typical and most prominent for horizontal layers, but not for films with vertical layers under similar processing conditions. Scattering instabilities (layer breakup) became more prominent as the number of layers increased with horizontal layers, but not for vertical layers. Both horizontally and vertically layered sheet showed curving of the layer interfaces. Curving was prominent in films with vertical layers and produced encapsulation of the vertically-layered structure by one of the materials. Figure 2 shows a multi-layer film with horizontal layers and Figure 3 shows a vertical layered material with instabilities.

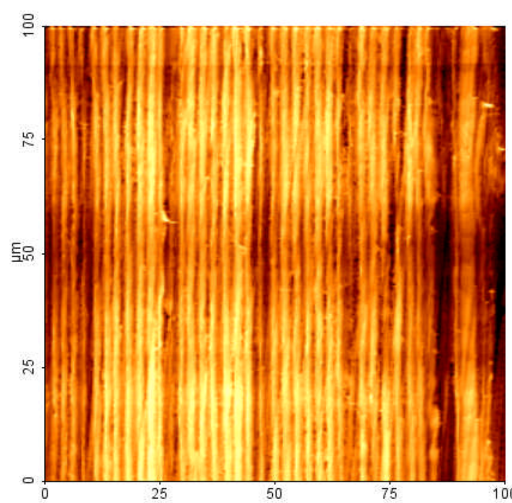



Figure 2: Horizontal nanolayered polymer film produced by multilayer co-extrusion.

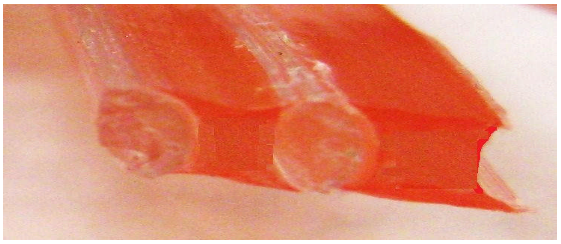


Figure 3: Vertical layered film showing curved layer interfaces.

## 2.3 Directed Assembly of Polymers

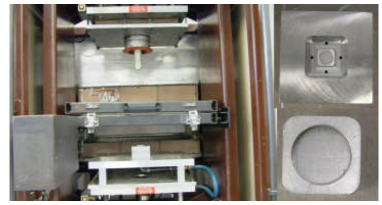
Directed assembly is an attractive process to prepare nonuniform nanoscale structures. We have developed a suite of templates and assembly processes for achieve high-rate nanomanufacturing. These assembly processes utilize electric fields and/or chemical functionalization. For a variety of applications, a second transfer step can be included.

Nanopatterned polymers are attractive for applications requiring nanoscale flexible structures such as the fabrication of: optoelectronic devices,[24] biosensors [25], flash memory devices,[26] quantum dots,[27] and templates for nanolithography applications.[28] Many of these applications need polymer structures that are patterned in non-uniform geometries, for example, complex geometries, such as sharp 90º bends, jogs, and T-junctions, are required for integrated circuit layouts [29].

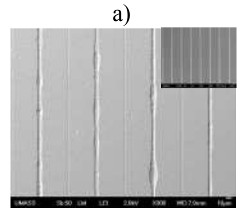
Polymer blends are particularly attractive for these types of applications, since blending two commercially available polymers is more cost efficient and offers a wide range of materials. Polymer blends also provide facile patterning into non-uniform geometries and allow preparation of patterns with multiple length scales in a single substrate (or operation). Polymer blends have been used for producing polymer nanostructures by directed assembly onto chemically functionalized patterns into both uniform and non-uniform patterns.[30,31]

Polymer blends can be patterned in a two step process, where the polymer is assembled and the pattern transferred in a second step. Alternatively, a polymer blend solution can be patterned directly onto chemically functionalized substrates.

Electrostatically addressable templates can be used to pattern conducting polymers and other nanoelements, such as carbon nanotubes. This can be followed by a process to transfer the pattern to a secondary flexible substrate. In particular, conducting polymers and carbon nanotubes can be assembled and transferred to a nonconducting material using melt based processes, such as thermoforming. (Figure 4)



a)



b)

Figure 4: a)thermoforming machine with mold and insert used for transfer, b)conducting polymer transferred to polyurethane sheet.

Alternatively, the polymers can be patterned directly from a solution containing a polymer blend onto a chemically functionalized surface. In this case the polymer is attracted to a specific site on the template surface by chemical attraction. This allows the fabrication of patterned polymer blends into a variety of nonuniform sturctures, including multiple length scales on a single substrate. (See Figure 5)

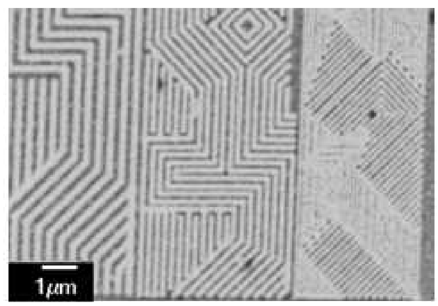



Figure 5: Polystyrene and polymethyl methacrylate patterned into nonuniform geometries and multiple length scales on a single template

## 3 CONCLUSIONS

Polymer materials are attractive for nanomanufacturing because of their ease of processing, light weight and flexibility. A variety of processing techniques can be used to fabricate nanostructures, such as blending with nanofiller, multilayer coextrusion, and directed assembly. Applications include lightweight structural components, EMI shielding materials, and flexible electronics.

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