

Scalable Polymer Patterning (SP²)

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ABSTRACT

Polymeric materials are easily fabricated into a wide array of structures for numerous applications. The bulk properties can be tailored for preparing novel structures and substrates for use as substrates for 3D printing. Particularly, the ability to tailor the surface for specific applications or enabling the printing of structures onto the substrate. For example, the surface chemistry and structure can be tailored for superhydrophobic or omniphobic properties. A process that is easily scaled to a continuous or large area structure is critical for commercialization and this work demonstrates scalable polymer patterning for creating superhydrophobic surfaces and tailored surfaces for controlling the printing of secondary structures by patterning of hydrophobic and hydrophilic surface patterns. In contrast to other manufacturing approaches, the processes described 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 polymer patterning 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. Unique structures for flexible electronic devices, metamaterials (near-IR and microwave), structural nanocomposites, icephobic surfaces or biocompatible materials will be described.

Keywords: directed assembly, superhydrophobic, nanostructures

1 INTRODUCTION

Nanotechnology offers unprecedented potential for many new high performance products. For example light weight enhanced materials, sensors with improved sensitivity, novel medical products, and new electronics devices. Fabrication of these devices is dependent on new nanomanufacturing approaches and new substrates on which place the nanomaterials. Nanomanufacturing processes have emerged in different areas, including biological systems^[1] and polymer nanocomposites electronics^[2]. From a fabrication perspective, printing is an attractive method to create new structures. Polymers are

attractive for printing and for substrates for subsequent printing. Polymers are light in weight, have a range of material properties, and can be processed at high rates and low temperatures. The printing approaches are based on directed assembly of nanoelement, such as conducting polymers^[3] or nanotubes^[4]. After printing, the assembled structures can be transferred to a polymer substrate. Patterning of two polymers can also be accomplished. For example the printing of two polymers (polymer blends) into uniform or nonuniform micro and nanoscale designs^{[5],[6],[7]}. The printing can be scaled to a continuous or roll to roll process.

Fabrication of novel, designer substrates is also possible. These substrates can be used to transfer the printed structure. For example twin screw extrusion to make nanocomposites^[8] and multi-layer films by extrusion^{[9],[10],[11]}. These novel substrates can be used in conjunction with the printing process to prepared unique structures, such as conducting polymers on an insulating polymer substrate for metamaterials or flexible electronics. The substrates can also be tailored to have specified properties in designs, such as hydrophilic areas to enable printing of materials and superhydrophobic in other areas to resist adhesion. Novel designer substrates are enabled by use of a variety polymer nanomanufacturing methods.

2 SCALABLE POLYMER PRINTING

2.1 Printing of nanoscale structures

Nanoscale designs, such as patterned polymers can be used for applications in biosensing^[12] or metamaterials. Nonuniform patterns and geometries using polymers or nanoelements and polymers are needed for layouts for integrated circuits^[13]. Nanoelements, such as carbon nanotubes, nanoparticles, etc. can be patterned by directed assembly. Either electric fields or chemical attraction can be used to assemble the nanoelements. This step can be considered similar to an inking process. A template, which will have the print design is used to “ink” the material and will vary in design and type depending on what is to be patterned.

For patterning of nanoelements, electric fields are an attractive method to pattern conducting materials. The approach can be used in a roll to roll process to assemble nanoelements, followed by transfer to a heated sheet.

Polymer blends can be patterned into a variety of nanoscale structures, which is attractive since blending two commercially available polymers is cost effective and offers a range of materials. Nonuniform geometrical patterning and fabrication of multiple length scale patterns on a single substrate are also possible. 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 in a single step process. Figure 1 shows an example of a unique pattern fabricated by this approach

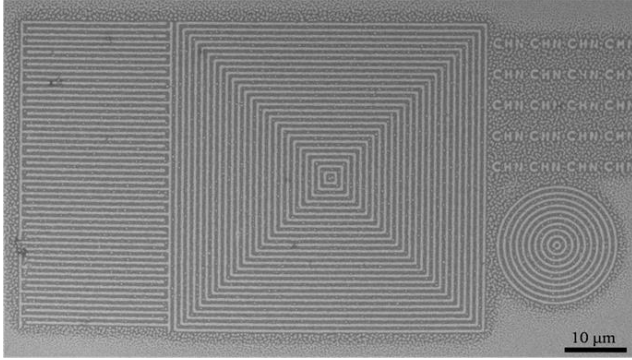


Figure 1: Nonuniform structures from directed assembly of polymer blends.

In the two step process, a nanoelement, such as nanoparticles, nanotubes, or conducting polymers, is patterned using electric fields. (The inking process) In a subsequent step the patterned nanoelement is transferred to a secondary substrate, in this case a flexible polymer. Of particular interest is the use of pulsed electrophoresis (pulses the electric current in on and off cycles) to increase template durability^[14]. The duration of current on/off time can be varied depending on the specific material to be patterned. For example a conducting polymer can be patterned onto a template with a 50% reduction in the heat build-up in the template. The transfer can occur using a simple solution casting method to apply the polymer film, but melt based processes, such as thermoforming are preferred and have been used to transfer MWNTs^[15] and a conducting polymer. In this approach, the assembled nanoelements (CNTs) on the template and heated polymer substrate come in contact using pressure and vacuum.

Recent work illustrates^{[16],[17]} rate-dependent adhesion as the critical for the kinetically controlled transfer printing approach. In this work we investigated the intrinsic mechanism of the transfer printing process and the effect of material properties on the transfer. The solution casting transfer process was used to eliminate the influence of temperature and contact pressure.

Creton, et al.^[18] illustrated the importance of entanglements to the strength of an interface between the immiscible polymer layers. Zhang, et al.^[19] considered the

strength of interface (G_c) to be proportional to the density of entanglements in the interface (Π). This depends on the Flory-Huggins interaction parameter and the distance between entanglements, and statistical segment length^[20].

Polyaniline emeraldine base (PANi) (Mw, 65 000 g/mol), (1s)-(t)-10-camphorsulfonic acid (CSA), PANi and CSA with a weight ratio of 1:1 were dissolved in DMF to make a solution of 1% weight concentration. The template consisted of nanoscale gold wires on a silicon dioxide wafer, fabricated by the e-beam lithography process. The assembly time, voltage, frequency and pattern size were varied to investigate the effect of these parameters on the assembly process. The assembled PANi was transferred to polymer films using solution casting. For this process 10 wt.% solution of polymers was cast onto the templates. The transfer is dependent on the critical binding strength of PANi-gold electrode ($G_c^{PANi-Gold}$) and the interface layer strength between the PANi and the polymer films ($G_c^{PANi-Film}$). The transfer of PANi from the template to the film happens when $G_c^{PANi-Film} > G_c^{PANi-Gold}$.

The strength of the interlayer ($G_c^{PANi-Film}$) is proportional to a_1 / bL_e^2 . The calculated result of a_1 / bL_e^2 are listed in Table 1. The calculated values matched well with the transfer result – the stronger adhesion improved the transfer of PANi from the template to polymer film. The value of a_1 / bL_e^2 is controlled by the difference between the solubility parameters (δ) of PANi and polymer substrates. The closer the solubility parameters of PANi and the polymer implies a higher value of a_1 / bL_e^2 , and higher adhesion between PANi the polymer substrates.

Table 1: List of L_e , solubility parameters and a_1 / bL_e^2 values for polymer films and PANi.

Polymer	L_e (nm)	δ (MPa ^{1/2})	a_1 / bL_e^2 (1/nm ²)	Transfer result
PANi		22.2		
PU	4.01	22.9	4.42+11	Transferred
PET	4.00	22.0	1.56E+12	Transferred
PS	7.65	18.7	2.43E+10	Non-transfer
PMMA	6.70	18.7	3.17E+10	Non-transfer
NBR	5.47	21.0	1.39E+11	Transferred
SEBS	6.07	16.0	2.18E+10	Non-transfer
Polyisoprene	4.74	17.5	3.87E+10	Non-transfer

The transfer process can be scaled to a roll to roll process (Figure 2). In the roll to roll process. In this case the transfer depends on the belt speed. The transfer also

depends on the 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.

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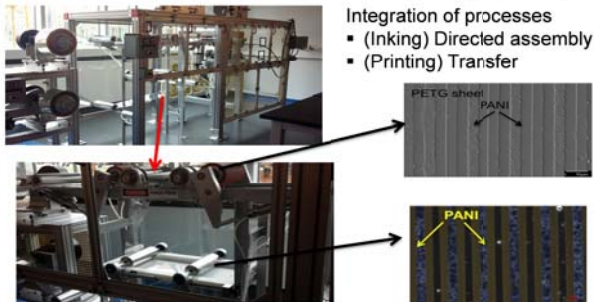


Figure 2: Experimental setup for roll to roll processing.

The continuous offset printing process can be used to fabricate unique structures such as chiral metamaterials (Figure 3).

Directed Assembly of a Chiral Metamaterial

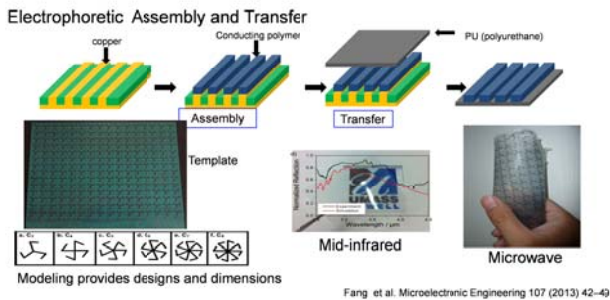


Figure 3: Experimental setup for roll to roll processing.

2.2 SUBSTRATES

2.2.1 Nanocomposites

Polymers can be often mixed with nanoscale fillers (polymer nanocomposites) to improve properties with low loadings. Nanocomposites are fabricated using melt-mixing, which does not use solvents and is more industrially compatible. Melt mixing is industrially compatible and is typically done in a twin screw extruder. This is a continuous process that has been used to fabricate a wide range of different nanocomposites using different fillers and polymers. The mixing process disperses the agglomerated nanoparticles. The properties of the nanocomposite are dependent on the filler level, dispersion (final particle size), distribution (consistency of composition), and any orientation (fibrous fillers). Control of the processing parameters is critical for obtaining the desired properties. In a twin screw process, polymer and nanoparticles are fed into the twin screw extruder, polymer

is melted and the filler mixed into the polymer (Figure 4). Mixing is controlled by process variables, such as, residence time, melt temperature, screw speed, etc. The materials made by this method can be fabricated into a variety of shapes using typical plastics processing methods. Extrusion of the nanocomposite can provide a sheet for subsequent printing or transfer. Thus, nanocomposites can be used as designer substrates in an offset printing process providing unique material configurations.



Figure 4: Example of twin screw equipment.

2.2.2 Multi-layer Coextruded Films

Coextrusion processes combine two polymer melts to produce unique films. This process has been used to prepare multilayer films for improved properties, including barrier and toughness^{[21],[22]}. The melt streams are split and stacked with the number of layers increasing with each splitting and stacking sequence. Typically horizontal layers are produced in the multilayer films, but vertical layers are also possible. Vertical layers appear as different materials across the width of the film, while a single material spans the thickness of the film (See Figure 5). In horizontal layers the material spans the width of the film. These multilayer films can include nanocomposites by using the mixing process described above.



Figure 5: Vertically layered polymer film produced by multilayer co-extrusion.

The printing process can be generalized to consider the inclusion of both novel substrates and printing of structures (Figure 6)

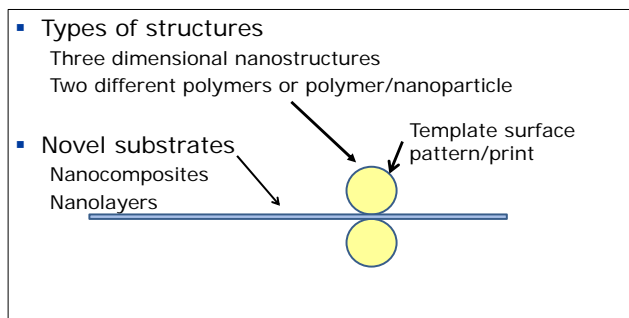


Figure 6: Printing and novel substrates

3 CONCLUSIONS

Polymer materials offer potential for nanomanufacturing applications because of their processing ease, light weight and flexibility. Fabrication of patterned polymer structures can be accomplished by a nanoscale offset printing approach based on directed assembly and transfer. The approach can be scaled to a roll to roll process. Substrates can be prepared from nanocomposites by continuous mixing, and multi-layer extrusion. The novel substrates can be used for printing of novel structures.

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REFERENCES

[1] M. Park, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Science* 1997, 276, 1401-1404.
 [2] Yang, C. H.; Shin, T. J.; Yang, L.; Cho, K.; Ryu, C. Y.; Bao, Z. N. *Adv. Funct. Mater.* 2005, 15, 671.
 [3] Jia Shen, Ming Wei, Mark Lawrence, Ryan Hoffman, Carol Barry and Joey Mead, Society of Plastics Engineers Annual Technical Conference 2008.
 [4] Arun Kumar, Ming Wei, Carol M. F. Barry, Stephen Orroth, Ahmed Busnaina, and Joey Mead, Society of Plastics Eng. Ann. Tech. Conf., May, 2008.
 [5] Liang Fang, Ming Wei, Carol Barry, and Joey Mead, *Macromolecules*, 2010, 43 (23), pp 9747-9753.
 [6] Chiota, J., Shearer, J., Wei, M., Barry, C. and Mead, J. (2009), *Small*, 5: 2788-2791

[7] Wei, M. L. Fang, J. Lee, S. Somu, X. Xiong, C. Barry, A. Busnaina, and J. Mead, *Advanced Materials*, 21(7), 735-832 (2009).
 [8] D. Kang, D. Kim, S.-H. Yoon, D. Kim, C. Barry, J. Mead, *Macromol. Mater. Eng.* 2007, 292, 329-338.
 [9] E. Nakamura, C. Barry, E. Cohen, J. Mead, M. Ogale, S. Orroth, R. Soni, *Proceedings, Soc. Plastics Eng. ANTEC 2010*, Orlando, FL, May 18-20, 2010, p. 2019.
 [10] E. Nakamura, C. Barry, E. Cohen, J. Mead, M. Ogale, S. Orroth, R. Soni, *Proceedings, Soc. Plastics Eng. ANTEC 2010*, Orlando, FL, May 18-20, 2010, p. 2037.
 [11] K. Ho, J. S. Lee, N. Viriyabanthorn, C. Sung, C. M. F. Barry, and J. L. Mead, *Proceedings of Society of Plastics Engineers Annual Technical Conference '04*, Chicago, IL, May 16-20, 2004, p. 376.
 [12] Gallant, N., Charest, J., King, W., Gracia, A., *J. Nanosci. Nanotechnol.*, 7:803-807 (2007).
 [13] Stoykovich, M., Kang, H., Daoulas, K., Liu, G., Liu, C., Pablo, J., Muller, M., Nealey, P., *ACS Nano*, 1:168-175 (2007).
 [14] Kumar, A., Kazmer, D., Barry, C., Mead, J., *Nanotechnology*, 23(33):1-11 (2012).
 [15] Kumar, A., Wei, M., Barry, C., Orroth, S., Busnaina, A., Mead, J., "Transfer of Template Patterned Carbon Nanotubes to a Polymer Surface Using the Thermoforming Process," *ANTEC Conf. Proceedings*, 968-972 (2008).
 [16] Meitl, M. A.; Zhu, Z. T.; Kumar, V.; Lee, K. J.; Feng, X.; Huang, Y. Y.; Adesida, I.; Nuzzo, R. G.; Rogers, J. A., *Nat. Mater.* 5, (2006) 33-38.
 [17] Xue Feng, Matthew A. Meitl, Audrey M. Bowen, Yongyang Huang, Ralph G. Nuzzo, and John A. Rogers, "Competing Fracture in Kinetically Controlled Transfer Printing" *Langmuir*, 23, (2007), 12555-12560.
 [18] Creton, C.; Kramer, E. J.; Brown, H. R.; Hui, C. Y. "Adhesion and Fracture of Interfaces between Immiscible Polymers: from the Molecular to the Continuum Scale" *Adv Polym Sci* 156 (2001), 53-136.
 [19] Jianbin Zhang, Timothy P. Lodge, Christopher W. Macosko, "Models for Adhesion at Weak Polymer Interfaces" *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 47, (2009) 2313-2319
 [20] Cole, P. J.; Cook, R. F.; Macosko, C. W. "Adhesion between Immiscible Polymers Correlated with Interfacial Entanglements" *Macromolecules* 36, (2003) 2808-2815.
 [21] Dooley, J. and Ramanathan, R., *Proc. Ann. Tech. Conf. Soc. Plast. Eng.*, 40, 89-93 (1994).
 [22] Vlcek, J., Kopytko, W., Zatloukal, M., and Birrane, T., *Proc. Ann. Tech. Conf. Soc. Plast. Eng.*, 128-131 (2005).