Expanding the Applicability of FDM-type Technologies Through Materials Development

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Abstract

Currently, the most common form of additive manufacturing is material extrusion 3D printing (ME3DP) based on fused deposition modeling (FDM®) technology which relies upon a thermoplastic monofilament as a base material for the fabrication of three dimensional objects. The dependence on thermoplastics as a feedstock by ME3DP platforms limits the applicability of this additive manufacturing method. A clear-cut path towards greater applicability is the introduction of novel materials with diverse physical properties which maintain compatibility with 3D printing platforms based on FDM® technology. The work in this paper presents efforts in the development of polymer matrix composites (PMC)s and polymer blends based on acrylonitrile butadiene styrene (ABS) and polycarbonate (PC), two thermoplastic materials commonly used by FDM®-type platforms. Mechanical testing and fractography via scanning electron microscopy (SEM) were the two main metrics used to characterize these new material systems. Overcoming barriers to the manufacturing of these novel 3D-printable materials systems is also presented.

Key Words: 3D Printing; Materials Characterization; Polymer Matrix Composites

Introduction

The evolution of additive manufacturing (AM) from a tool used to rapidly create three dimensional models into to a fully developed technique capable of fabricating multifunctional devices has undergone significant advancements in recent years. One driving force of significant innovation has been the hybridization of AM with other manufacturing techniques such as direct write (DW) where conductive and insulating materials are deposited enabling the creation of "structural" electronics. There are several examples of these novel electronic devices where DW was combined with stereolithography (SLA); pushing the forefront of what is possible using AM [1-5].

While such achievements help to advance the field of AM to greater heights in applicability and benefit to society, 3D printing platforms must rely, for the most part, on "off the shelf" material systems. For example, there is a large body of work pertaining to characterization of titanium alloys (typically Ti 6Al 4V) as used in electron beam melting (EBM) and selective laser melting (SLM) [6-9]. So too are there many instances of the characterization of acrylonitrile butadiene styrene (ABS) for use in FDM applications. However, by allowing a given platform access to materials with a diverse set of physical properties, the possibility to fabricate all-3D-printed, multi-functional structures becomes reality. One such example is the Objet material jetting AM platform which can print either epoxy or elastomeric materials. This enables the printing of objects with both flexible and rigid sections, and has led to the ability to fabricate actuators and other objects which can take advantage of rigid and flexible members such as mechanical actuators among others [10, 11].

The work presented in this paper demonstrates the development of application-specific material systems meant for use in material extrusion 3D printing (ME3DP) platforms through the creation of novel polymer matrix composites (PMC)s and polymer blends (PB)s. The new material systems with three intended applications: 1) the application of ME3DP in electromagnetic and electromechanical uses; 2) the application of ME3DP in austere environments; and 3) the application of ME3DP itself. The third goal was geared towards the development of materials which mitigate issues associated with ME3DP such as build orientation-related mechanical property anisotropy— an issue documented in the use of nearly every AM platform [12-24]— as well as aspects other such as surface finish.

The strategy employed by our group, to further the applicability of ME3DP, has been the creation of PMCs and PBs based upon a known printable material such as ABS or polycarbonate (PC). The common theme found between the fabrication of PMCs and PBs is the taking advantage of the physical properties of two or more materials, which have been blended together in some way.

In general, the equation describing a composite is typically given in terms of yield strength:

$$\sigma_c = V_{fm}\sigma_m + V_{fr}\sigma_r, \tag{1}$$

where σ_c is the yield strength of the composite, V_{fm} is the volume fraction of the matrix(in our case ABS or a similar thermoplastic), V_{fr}, is the volume fraction of the reinforcing agent, σ_m is the ultimate tensile strength of the matrix and σ_r is the ultimate tensile strength of the reinforcing agent.

While there are several parameters of a material which can be tailored by polymer blending, an example of blending two polymers in order to manipulate glass transition temperature (T_g) comes in the form of the Fox equation [25]:

$$\frac{1}{T_{g\,blend}} = \frac{x_1}{T_{g1}} + \frac{x_2}{T_{g2}}, \tag{2}$$

where x_1 and x_2 are the weight fraction of the individual polymers and T_{g1} and T_{g2} represent the glass transition temperatures of the two polymers in a blend. An example of a polymer blend used in FDM is Ultem 9085 which is a blend of polyetherimide (T_g = ~216 °C) and PC (T_g = ~147 °C). In this example, Ultem 9085 has a lower T_g (~186 °C) compared to polyetherimide alone due to the addition of PC. As will be seen in this work various representations of the rule of mixtures such as equations 1 and 2 are the lynchpin to increasing the diversity in physical properties of 3D printable materials.

Experimental Procedure

All PMCs and blends were fabricated through the use of a Dr. Collin twin screw extruder / compounder (Model ZK 25T, Dr. Collin GmbH, Ebersberg, Germany) which was designed to fabricate a monofilament 1.75mm in diameter. Each material system necessitated specific machine properties which can be found in previously reported work [18, 26]. Mechanical testing was carried out through the use of an Instron® 5866 tensile test machine (Instron, Norwood, MA). Tensile test specimens were printed using a MakerBot Replicator (MakerBot Industries, Brooklyn, NY) following dimensions specified in the ASTM D638-10 based on the Type V parameters [27]. Fractography was performed on the fracture surfaces of tested specimens by analyzing micrographs obtained from a scanning electron microscope (SEM). The SEM used in this study was a Hitachi TM-1000 Tabletop SEM equipped with a backscatter electron detector and operating with an accelerating potential of 15 kV (Hitachi High-Technologies Europe GmbH, Germany). As we were examining polymeric specimens, a preliminary sputter coating with an Au/Pd alloy was necessary and carried out through the use of a Gatan coating system (Model 682, Gatan, Inc., Pleasanton, CA).

Electromagnetic and Electromechanical Applications

Additive Manufacturing has proven to be a key enabler for the creation of metamaterial devices due to the ability to fabricate complex anisotropic and spatially variant geometries [28, 29] as seen in Figure 1. The major drawback to the use of AM in this application is the electromagnetic (EM) properties of the feedstock material, namely the dielectric constant— which is ~2 to 3 for most thermoplastics. Analogous to increasing the yield strength of a polymer through the addition of carbon or glass fibers, the dielectric constant of a polymer can be increased through the addition of materials composites (metal oxides for example) with a greater relative permittivity. Many equations have been developed to model the dielectric constant of a mixture; one being the Maxwell Garnett equation [30]:

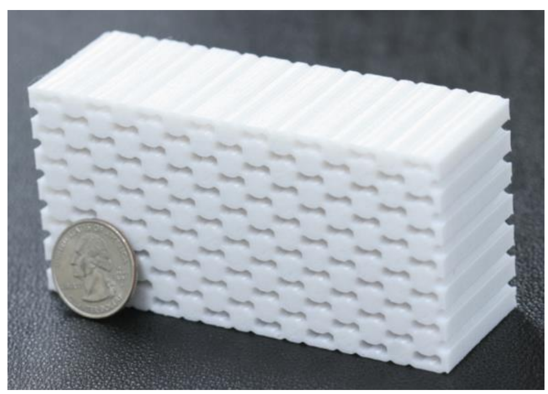

Figure 1. 3D printed anisotropic metamaterial [28].

$$\frac{\varepsilon-\varepsilon_1}{\varepsilon+2\varepsilon_1} = \delta_0 \frac{\varepsilon_0-\varepsilon_1}{\varepsilon_0+2\varepsilon_1}, \quad (3)$$

where ε is the permittivity of the mixture, ε_1 is the permittivity of the matrix, ε_0 is the permittivity of the additive material, and δ_0 is the volume fraction of the additive material.

Work by our group has dealt with the blending of ABS and PC with TiO_2 (ε=50) in the development of printable materials geared for EM applications. One problem encountered was achieving dispersion of the additive within the matrix. We found it necessary to functionalize TiO_2 in a process involving a Silane agent (purchased from Sigma-Aldrich) geared for either PC or ABS which resulted in smaller agglomerations and better general dispersion (Fig. 2).

Another application which stands to befit from the availability of printable materials with a wider range of physical properties is the 3DP printing of an electric motor (Fig. 3) as demonstrated by Aguilera *et al.* [31]. Were the core of the motor to be printed from ferromagnetic materials, the power of the motor would be increased. En route to achieving this goal, we have developed printable ferromagnetic composites based on either PC or ABS (Fig. 3)

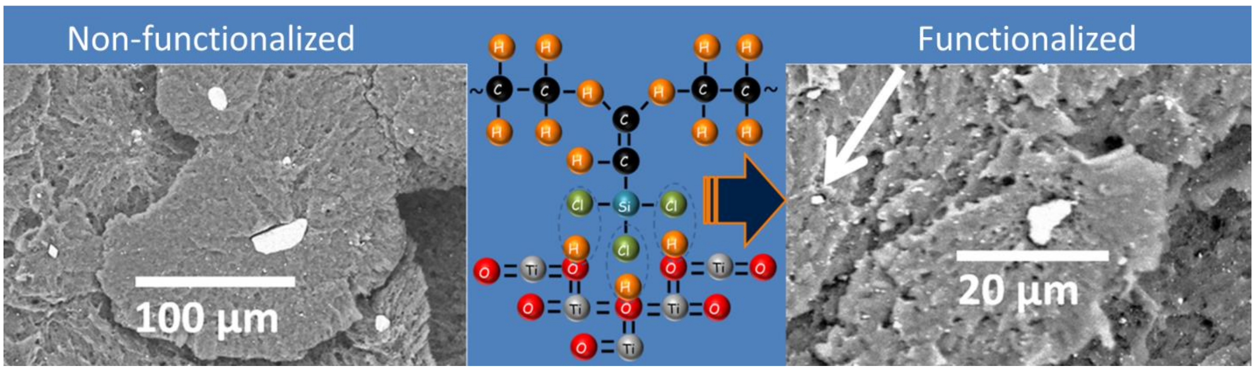

Figure 2. Functionalizing TiO2 prior to compounding with ABS led to better dispersion within the polymeric matrix.

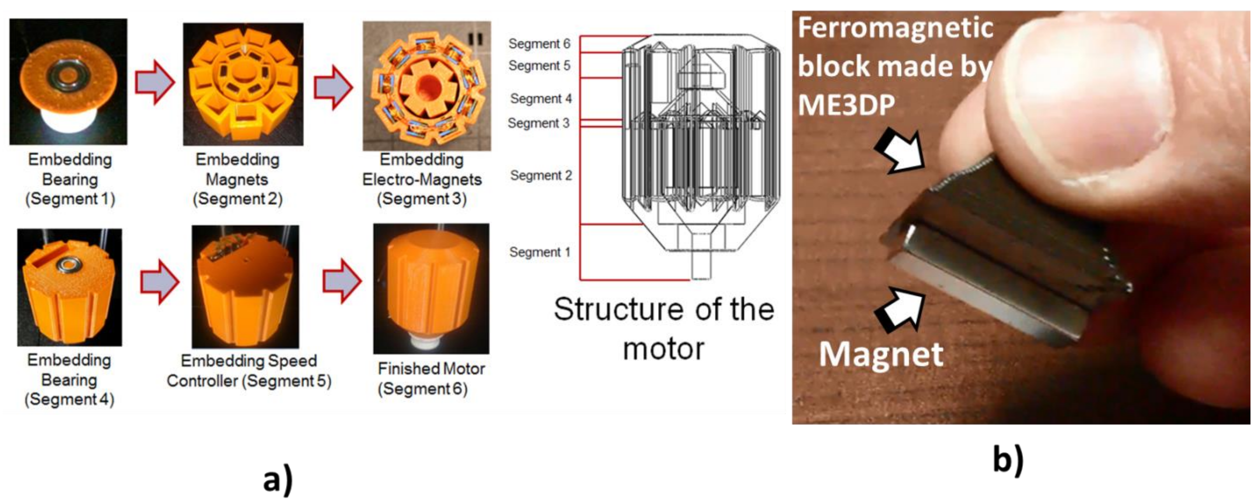

Figure 3. a) The process of fabricating a 3D printed motor. From reference [31]. b) 3D-printable ferromagnetic material which could be used to enhance the motor's performance.

<u>Applications in Austere Environments</u>

In order for space-based and remote research outposts to effectively utilize ME3DP, the implementation of a closed-loop manufacturing scheme is needed where printed parts can be reprocessed into a 3D printer-compatible monofilament. This practice would enable more 3D printed structures from the same amount of base materials and allow for the reprocessing of short lifespan or misprinted parts; requiring less material to be transported to a given production site. However, a concern for such a material recycling process is the thermomechanical degradation which will result in decreased mechanical strength [32].

There has also been significant investigation of the effect of additives on the thermomechanical degradation of ABS. Here the additives investigated were ZnO nanorods, TiO2 nanoparticles, and a palygorskite organo-nanoclay pigment marketed as MayaCrom® blue. ABS-based PMCs created from each of the three additives were prepared and printed as tensile test specimens. The specimens were tested, reprocessed into a monofilament, and then used to print another second set of tensile specimens. The process was then repeated for two recycling cycles. As can be seen in Fig. 4, the addition of 2% by weight ZnO nanorods demonstrated the most promise in the reduction of thermomechanical degradation due to reprocessing.

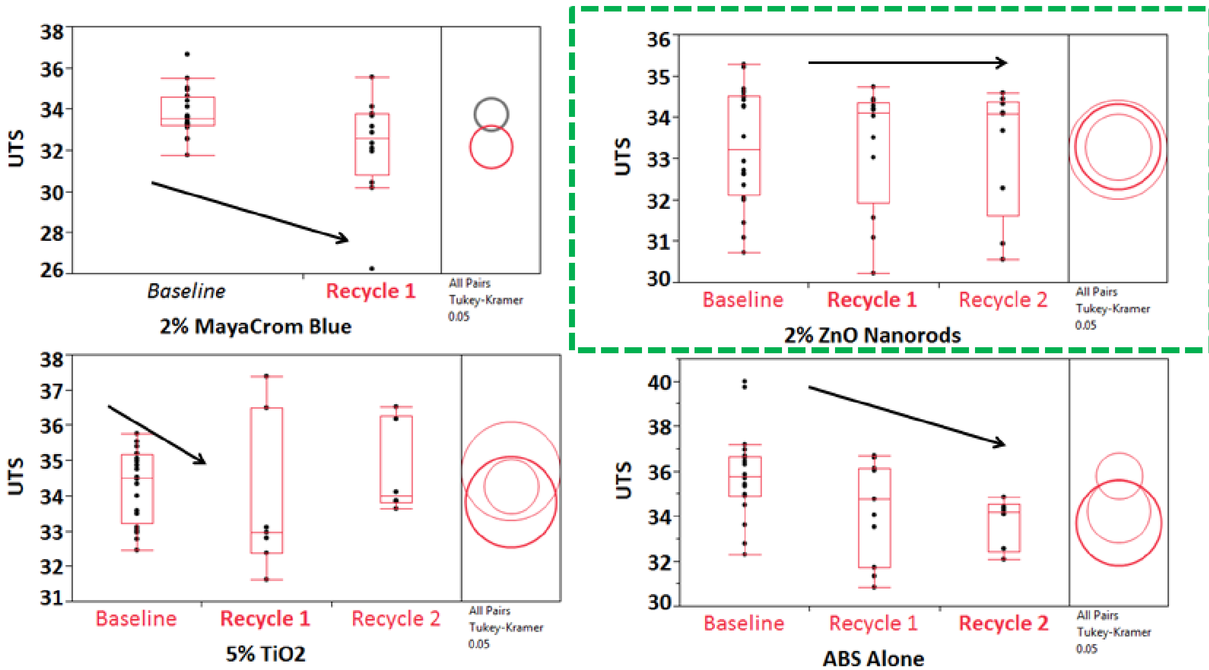

Figure 4. Results of thermomechanical degradation testing on ABS-based composites. Here ZnO nanorods demonstrated the most promise in the mitigation of thermomechanical degradation.

Of particular interest to space-based manufacturing is the ability to print materials with radiation shield capability. One metric to test this ability is testing of the transmittance of x-rays through a material. The intensity of x-rays which pass (or are transmitted) through a material of a given thickness, x, can be calculated based on the following equation [33]:

$$I_x = I_o e^{-\left(\frac{\mu}{\rho}\right)\rho x}, \tag{4}$$

where I_o is the intensity of the x-rays before passing through the material and ρ is the density of the material. The parameter $\frac{\mu}{\rho}$ is known as the mass absorption coefficient and is pertinent to our development of application-specific PMCs as it can be manipulated through mixing similar to the other physical parameters discussed here as described by the equation [33]:

$$\left(\frac{\mu}{\rho}\right)_m = x_1\left(\frac{\mu}{\rho}\right)_1 + x_2\left(\frac{\mu}{\rho}\right)_2, \quad (5)$$

where the subscript m denotes mixture, x_1 and x_2 are the mass fractions of substance 1 and substance 2. It should also be noted that density plays a large role in the blocking of x-ray transmission as indicated by equation 4. In our case we chose to improve the x-ray impeding capability of PC through the addition of tungsten powder and a simple model to describe the density of our composite can be expressed by the equation:

$$\rho_c = x_1\rho_1 + x_2\rho_2, \quad (6)$$

which essentially demonstrates the manipulation of a PMC through the addition of dense material. Indeed it has been shown that even small amounts of tungsten can have a profound effect on the ability to block x-ray radiation transmission. Figure 5 shows the difference in x-ray transmission between 3D printed plates fabricated from PC and PC/ W PMCs loaded with 1%, 3% and 5% by weight tungsten, respectively.

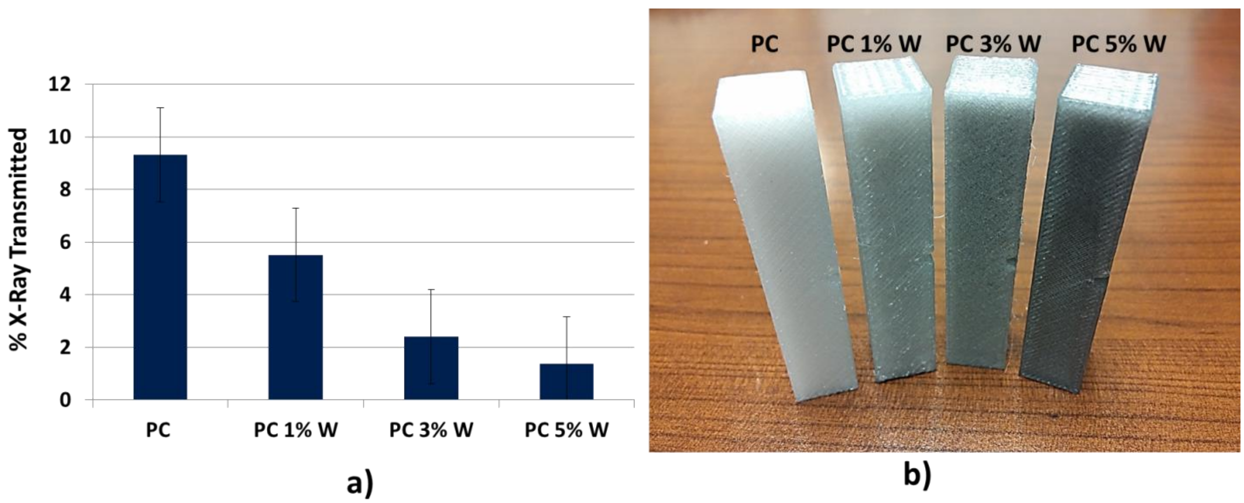

Figure 5. a)The ability to tailor the amount of x-ray transmission based on tungsten loading and b) 3D printed impact test specimens made from the same materials.

Materials for the Application of 3D Printing

As mentioned before; currently, the vast majority of manufacturing based on 3D printing relies on traditional or "off the shelf" material systems. While there are examples of the development of novel materials geared towards the 3D printed fabrication of novel devices, there remains a need for the development of materials geared specifically for 3D printing.

The development of 3D-printer-specific material systems should be directed towards those that mitigate issues associated with a given 3DP process. As mentioned before, an issue encountered by nearly every AM process is mechanical anisotropy based on build orientation. Initial characterization of the effect on additives on build orientation anisotropy was presented in Torrado Perez *et al.* [18] where a blend of ABS and 5% by weight styrene ethylene butadiene styrene (SEBS) was shown to decrease the difference in ultimate tensile strength (UTS) between samples printed in the XYZ and ZXY directions.

Further development of binary and ternary ABS-based PBs has been presented by Rocha *et al*.[26] where it was shown that a ternary blend of ABS, ultra-high molecular weight polyethylene (UHMWPE) and SEBS in a by weight ratio of 75:25:10 was shown to be able to print smoother inclined planes as compared to ABS alone. Analysis via scanning electron microscopy (SEM) revealed that the rheology of this ternary PB led to an intermingling of the print rasters as seen in Figure 6. The rheological differences altered the deposition characteristics as compared to ABS and allowed for the printing of smoother planes.

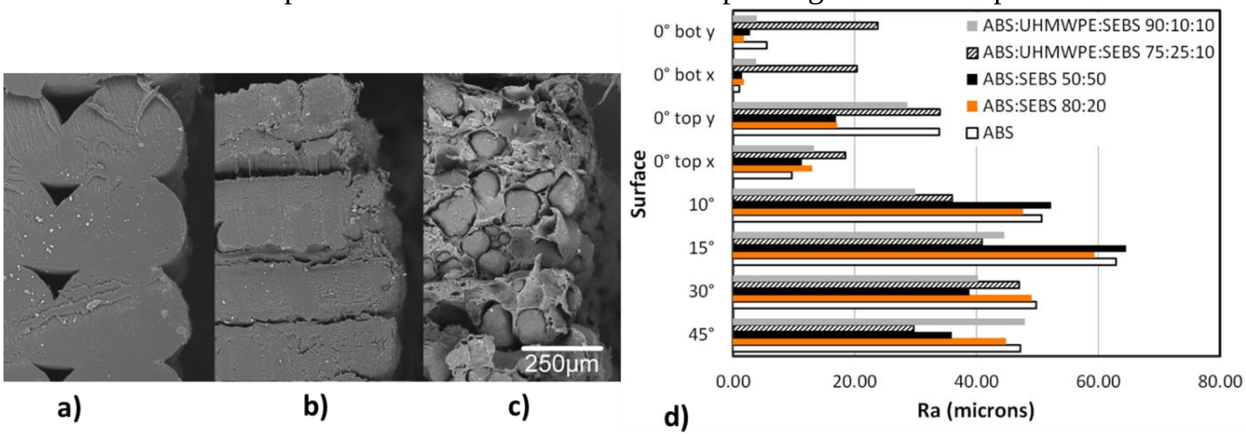

Figure 6. SEM images of cross sections of a) ABS, b) ABS:SEBS 50:50 blend and c) ABS:UHMWPE:SEBS 75:25:10. Note the differences in print rasters. From [26] d) Corresponding surface roughness data from a test piece described in Rocha *et al.* [26] showing the ability of these novel blends to print smoother inclined planes.

The same blend has also proven to be an enabler for the improvement of anisotropy by decreasing the difference in UTS between samples fabricated in the XYZ and ZXY print directions [34] as is demonstrated in Figure 7. The reason for this decrease was shown to be due to the intermingling between print rasters as seen by the cross sections in Figures 6 and 7 and the fracture surfaces in Figure 8. While this blend does experience a dramatic decrease in UTS, as compared to ABS, it stands as a step towards the development of a material system geared specifically at mitigating an issue inherent to AM.

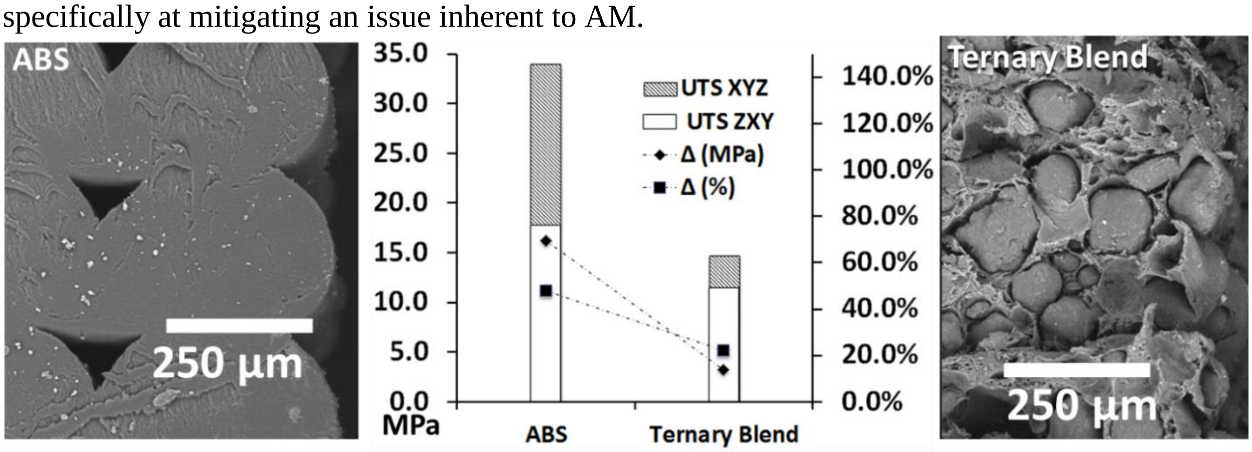

Figure 7. The rheological differences of the ternary blend as compared to ABS obscure the print rasters leading to a decrease in build orientation-caused mechanical property anisotropy [26, 34].

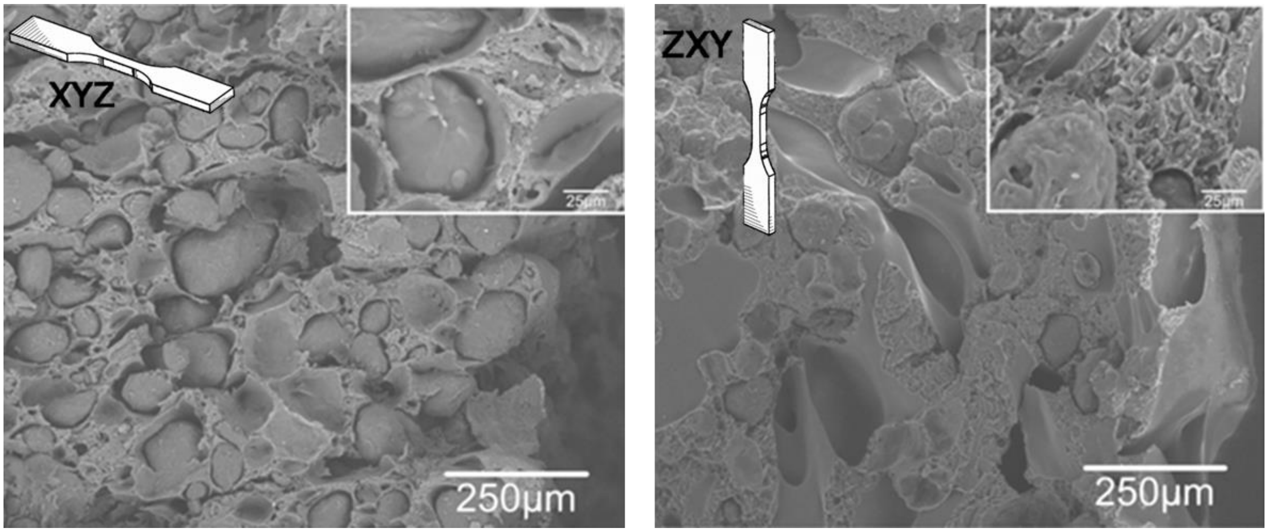

Figure 8. The intermingling in print rasters is also apparent on the fracture surfaces of tensile test specimens printed in different orientations from [34].

Conclusions

The work presented here demonstrates research efforts geared towards the development of 3D printable materials which are intended for specific applications involving material extrusion 3D printing. Through the development of novel polymer matrix composites and polymer blends, new materials have been fabricated which can be applied to: 1) 3D printing of electromagnetic and electromechanical components; 2) 3D printing in austere environments; and 3) material extrusion 3D printing. The strategy of utilizing known printable base materials has aided in maintaining printing compatibility with material extrusion 3D printing platforms.

Materials characterization efforts based on mechanical testing and SEM microanalysis have provided insight into the dispersion of additives, the rheological behavior of new material systems, and the fracture morphology. This information is critical in building a knowledge base for the development of new thermoplastic material systems for 3D printing. While the advances towards the creation of all-3D printed electronic, electromechanical, and electromagnetic devices will continue, the development of novel material systems remains a critical enabler for the future of additive manufacturing.

Acknowledgements

The work performed here occurred in the W.M. Keck Center for 3D Innovation and the Department of Metallurgical and Materials Engineering at The University of Texas at El Paso. The authors are grateful for the contributions of Joel English, Angel Torrado Perez, Carmen Rocha and Lauro Barbieri. This project was supported by a grant from the Intelligence Community Postdoctoral Research Fellowship Program through funding from the Office of the Director of National Intelligence under grant no. 2012-12071000005. All statements of fact, opinion, or analysis expressed are those of the author and do not reflect the official positions or views of the Intelligence Community or any other U.S. Government agency. Nothing in the contents should be construed as asserting or implying U.S. Government authentication of information or Intelligence Community endorsement of the author’s views. The authors are also grateful for additional support which came from the National Aeronautics and Space Administration (NASA) under grant no. 282002-8784.

References

[1] A. J. Lopes, E. MacDonald, and R. B. Wicker, "Integrating stereolithography and direct print technologies for 3D structural electronics fabrication," *Rapid Prototyping Journal*, vol. 18, no. 2, pp. 129–143, 2012.

[2] R. B. Wicker and E. W. MacDonald, "Multi-material, multi-technology stereolithography," *Virtual and Physical Prototyping*, vol. 7, no. 3, pp. 181–194, 2012.

[3] Navarrete M., Lopes A., Acuna J., Estrada R., MacDonald E., Palmer J., and Wicker R., 2007, Integrated layered manufacturing of a novel wireless motion sensor system with GPS, Proceedings of the 18th Annual Solid Freeform Fabrication Symposium, University of Texas at Austin, Austin, TX, pp. 575-585.

[4] Castillo, S., Muse, D., Medina, F., MacDonald, E., Wicker, R., 2009 "Electronics Integration in Conformal Substrates with Additive Layered Manufacturing," Proceedings of the 20th Annual Solid Freeform Fabrication Symposium, University of Texas at Austin, Austin, TX, pp. 730-737.

[5] DeNava E., Navarrete M., Lopes A., Alawneh M., Contreras M., Muse D., Castillo S., MacDonald E., and Wicker R., 2008, "Three-Dimensional Off-Axis Component Placement and Routing for Electronics Integration using Solid Freeform Fabrication," Proceedings of the 19th Annual Solid Freeform Fabrication Symposium, University of Texas at Austin, Austin, TX, , pp. 362–369.

[6] L. E. Murr, S. M. Gaytan, D. A. Ramirez, E. Martinez, J. Hernandez, K. N. Amato, P. W. Shindo, F. R. Medina, and R. B. Wicker, "Metal Fabrication by Additive Manufacturing Using Laser and Electron Beam Melting Technologies," *Journal of Materials Science & Technology*, vol. 28, no. 1, pp. 1–14, Jan. 2012.

[7] L. E. Murr, K. N. Amato, S. J. Li, Y. X. Tian, X. Y. Cheng, S. M. Gaytan, E. Martinez, P. W. Shindo, F. Medina, and R. B. Wicker, "Microstructure and mechanical properties of open-cellular biomaterials prototypes for total knee replacement implants fabricated by electron beam melting," *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 4, no. 7, pp. 1396–1411, Oct. 2011.

[8] L. E. Murr, S. A. Quinones, S. M. Gaytan, M. I. Lopez, A. Rodela, E. Y. Martinez, D. H. Hernandez, E. Martinez, F. Medina, and R. B. Wicker, "Microstructure and mechanical behavior of Ti–6Al–4V produced by rapid-layer manufacturing, for biomedical applications," *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 2, no. 1, pp. 20–32, Jan. 2009.

[9] K. Puebla, L. E. Murr, S. M. Gaytan, E. Martinez, F. Medina, and R. B. Wicker, "Effect of Melt Scan Rate on Microstructure and Macrostructure for Electron Beam Melting of Ti-6Al-4V," *Materials Sciences and Applications*, vol. 3, no. 5, pp. 259–264, 2012.

[10] J. P. Moore and C. B. Williams, "Fatigue Characterization of 3D Printed Elastomer Material," in *International Solid Freeform Fabrication Symposium*, 2012, pp. 641–655.

[11] J. Rossiter, P. Walters, and B. Stoimenov, "Printing 3D dielectric elastomer actuators for soft robotics," 2009, vol. 7287, p. 72870H–72870H–10.

[12] S.-H. Ahn, M. Montero, D. Odell, S. Roundy, and P. K. Wright, "Anisotropic material properties of fused deposition modeling ABS," *Rapid Prototyping Journal*, vol. 8, no. 4, pp.

248–257, Oct. 2002.
[13] A. Bagsik, V. Schoeppner, and E. Klemp, "FDM Part Quality Manufactured with Ultem* 9085," in *14th International Scientific Conference on Polymeric Materials, September*, 2010, vol. 15.
[14] A. Bellini and S. Güçeri, "Mechanical characterization of parts fabricated using fused deposition modeling," *Rapid Prototyping Journal*, vol. 9, no. 4, pp. 252–264, Oct. 2003.
[15] O. S. Es-Said, J. Foyos, R. Noorani, M. Mendelson, R. Marloth, and B. A. Pregger, "Effect of Layer Orientation on Mechanical Properties of Rapid Prototyped Samples," *Materials and Manufacturing Processes*, vol. 15, no. 1, pp. 107–122, 2000.
[16] R. Hague, S. Mansour, N. Saleh, and R. Harris, "Materials analysis of stereolithography resins for use in Rapid Manufacturing," *Journal of Materials Science*, vol. 39, no. 7, pp. 2457–2464, Apr. 2004.
[17] R. Hague *, S. Mansour, and N. Saleh, "Material and design considerations for rapid manufacturing," *International Journal of Production Research*, vol. 42, no. 22, pp. 4691–4708, 2004.
[18] A. R. Torrado Perez, D. A. Roberson, and R. B. Wicker, "Fracture Surface Analysis of 3D-Printed Tensile Specimens of Novel ABS-Based Materials," *J Fail. Anal. and Preven.*, vol. 14, no. 3, pp. 343–353, Jun. 2014.
[19] V. Vega, J. Clements, T. Lam, A. Abad, B. Fritz, N. Ula, and O. S. Es-Said, "The Effect of Layer Orientation on the Mechanical Properties and Microstructure of a Polymer," *J. of Materi Eng and Perform*, vol. 20, no. 6, pp. 978–988, Aug. 2011.
[20] B. Caulfield, P. E. McHugh, and S. Lohfeld, "Dependence of mechanical properties of polyamide components on build parameters in the SLS process," *Journal of Materials Processing Technology*, vol. 182, no. 1–3, pp. 477–488, Feb. 2007.
[21] A. Takaichi, Suyalatu, T. Nakamoto, N. Joko, N. Nomura, Y. Tsutsumi, S. Migita, H. Doi, S. Kurosu, A. Chiba, N. Wakabayashi, Y. Igarashi, and T. Hanawa, "Microstructures and mechanical properties of Co–29Cr–6Mo alloy fabricated by selective laser melting process for dental applications," *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 21, pp. 67–76, May 2013.
[22] L. E. Murr, K. N. Amato, S. J. Li, Y. X. Tian, X. Y. Cheng, S. M. Gaytan, E. Martinez, P. W. Shindo, F. Medina, and R. B. Wicker, "Microstructure and mechanical properties of open-cellular biomaterials prototypes for total knee replacement implants fabricated by electron beam melting," *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 4, no. 7, pp. 1396–1411, Oct. 2011.
[23] L. E. Murr, S. A. Quinones, S. M. Gaytan, M. I. Lopez, A. Rodela, E. Y. Martinez, D. H. Hernandez, E. Martinez, F. Medina, and R. B. Wicker, "Microstructure and mechanical behavior of Ti–6Al–4V produced by rapid-layer manufacturing, for biomedical applications," *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 2, no. 1, pp. 20–32, Jan. 2009.
[24] M. L. Griffith, D. M. Keicher, C. L. Atwood, J. A. Romero, J. E. Smugeresky, L. D. Harwell, and D. L. Greene, "Free form fabrication of metallic components using laser engineered net shaping (LENS)," in *Proceedings of the Solid Freeform Fabrication Symposium*, 1996, pp. 125–131.
[25] W. Brostow, R. Chiu, I. M. Kalogeras, and A. Vassilikou-Dova, "Prediction of glass transition temperatures: Binary blends and copolymers," *Materials Letters*, vol. 62, no. 17–18, pp. 3152–3155, Jun. 2008.

[26] C. Rocha, A. R. Torrado Perez, D. A. Roberson, C Shemelya, E. MacDonald, R. B. Wicker, Novel ABS-based Binary and Ternary Polymer Blends for Material Extrusion 3D Printing, Journal of Materials Research, 2014, Accepted In press.

[27] ASTM D638-10, "Test Method for Tensile Properties of Plastics," ASTM International, 2010.

[28] C. R. Garcia, J. Correa, D. Espalin, J. H. Barton, R. C. Rumpf, R. Wicker, and V. Gonzalez, "3D printing of anisotropic metamaterials," *Progress In Electromagnetics Research Letters*, vol. 34, pp. 75–82, 2012.

[29] R. C. Rumpf, J. Pazos, C. R. Garcia, L. Ochoa, and R. Wicker, "3D Printed Lattices with Spatially Variant Self-Collimation," *Progress In Electromagnetics Research*, vol. 139, pp. 1–14, 2013.

[30] E. C. Chan and J. P. Marton, "Generalized Maxwell Garnett equations for rough surfaces," *Journal of Applied Physics*, vol. 45, no. 11, pp. 5004–5007, Nov. 1974.

[31] E. Aguilera, J. Ramos, D. Espalin, F. Cedillos, D. Muse, R. Wicker, and E. MacDonald, "3D Printing of Electro Mechanical Systems." Proceedings of the 24th Annual Solid Freeform Fabrication Symposium, University of Texas at Austin, Austin, TX, Society of Manufacturing Engineers, pp. 950–961.

[32] R. Scaffaro, L. Botta, and G. Di Benedetto, "Physical properties of virgin-recycled ABS blends: Effect of post-consumer content and of reprocessing cycles," *European Polymer Journal*, vol. 48, no. 3, pp. 637–648, Mar. 2012.

[33] B. D. Cullity and S. R. Stock, *Elements of X-ray Diffraction*. Pearson, 2001.

[34] A. R. Torrado Perez, Y. Lin, D. A. Roberson and R. B. Wicker, Defeating anisotropy of mechanical properties in parts fabricated by material extrusion 3D Printing Through Novel Materials Development, Additive Manufacturing, 2014, Submitted.