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<th>The additive manufacturing of model polymer nanolaminates via automated spray deposition</th>
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ABSTRACT: Polymer nanocomposites represent a key addition to the palette of advanced polymeric materials available to us in the context of additive manufacturing. However, our understanding of their properties, and thus our ability to predict them and to design parts based on them, remains limited. With this in mind, nanolaminates have been formed via an additive process developed in our group and referred to as automated spray deposition; these materials have been characterized with the express purpose of better understanding the composition-structure-properties relations critical to our ability to create high performance polymeric materials by design via additive techniques. Here we present a preliminary comparison of the dynamic mechanical properties of two families of nanolaminates, essentially identical except for the polarity of the polymer phase and the strength of polymer / nanofiller interactions, with the aim of better understanding the mechanical response of such materials.

KEYWORDS: polymer, nanocomposite, nanolaminate, dynamic, mechanical

Additive manufacturing represents a technology of critical importance, promising to provide for a new era of customizability as far as part design is concerned. The development of a wide range of approaches to additive manufacturing has enabled its application to every major class of material. The most visible forms of additive manufacturing typically involve polymeric materials, given the relative ease of processing vs. metals and ceramics. While much work has been done in this field, however, in order to fully realize the potential of this technology, there is a clear need to improve materials properties.

In traditional plastics processing, we have many avenues open to us as far as properties enhancement is concerned. In additive manufacturing, however, our choices are typically much more limited. Flow behavior is critical, and because of the desire for high resolution, there is a constant push to reduce the minimum quantity of material that may be dispensed or deposited in the context of any additive manufacturing process. How are we to achieve the desired combination of rapid processing, physical and mechanical stability and multifunctionality in this context?

One answer lies in the addition of high aspect ratio nanofillers to form polymer nanocomposites. Nanofillers, when properly dispersed, represent one of the few reinforcement options that may be
readily applied to a broad range of additive manufacturing technologies, with their refined spatial
dimensions enabling them to pass where larger particles would cause clogging and arrest the process.
High aspect ratio nanofillers in particular provide a desirable combination of effective reinforcement
and shear thinning behavior, ensuring both performance and processability – as demonstrated by the
pioneering work of Compton & Lewis (2014) concerning the direct-write additive manufacturing of
polymer / nanoclay hybrids, for instance. Finally, polymer nanocomposites are capable of providing
a broad range of functionalities beyond simple mechanical reinforcement, from barrier properties to
flame retardance to desirable dielectric characteristics, to name just a few (Marquis et al, 2013).
However, in order to fully benefit from what such materials have to offer and to mate the dream of
materials by design with additive manufacturing, it is essential that we understand the means by
which their properties arise.

It is with this in mind that we present our efforts in the area of polymer nanolaminates. These
materials are themselves formed via an additive manufacturing process we term automated spray
deposition, whereby layers of material are deposited in succession to build up a macroscopic film or
sheet with a well-defined structure (Figure 1). In addition, their components have been selected and
their composition varied for the express purpose of elucidating the sorts of composition-structure-
properties relations essential to the creation of high performance 3D printed nanocomposite parts
with predictable properties.

Figure 1. Schematic of the automated spray deposition process; polymer and nanofiller in a common solvent are sprayed onto
the surface of a rotating drum covered with a polymeric release liner (at left), with each deposition cycle adding an
incremental amount of material. Once the desired thickness has been reached, the nanolaminate is removed from the drum as
a free-standing thin-film (at right).

We have previously reported on our efforts to prepare and characterize nanolaminates in-depth, and
have described the structure and properties of these materials in detail (Dunkerley et al, 2010, 2011
& 2015; Fillery et al, 2012). Briefly, these materials possess a so-called “bricks-and-mortar”
structure, with the high aspect ratio clay layers highly aligned in the plane of the film except at the
lowest clay concentrations studied.

From a scientific standpoint, polystyrene is a convenient material, easy to work with and well-
studied. From a practical standpoint, polystyrene and related styrenic polymers represent obvious
targets for 3D printing applications given their availability, attractive properties and amorphous
nature (critical for dimensional stability in this context). Indeed, this is why ABS is one of the most
frequently printed polymeric materials. Such polymers tend to be quite brittle, however, resulting in parts with relatively low toughness.

In this context, Eastman’s Tritan copolyester represents an ideal system for comparison. From a scientific standpoint, both polystyrene and the copolyester are transparent, amorphous plastics with glass transition temperatures of ~100°C. This and similar copolysters have been shown to produced intercalated structures with Cloisite 20A (Jafferji et al, 2012) in a similar fashion to polystyrene (see for instance Dunkerley et al, 2010, 2011 & 2015), but given its greater polarity, the copolyester is expected to exhibit stronger interfacial interactions with the nanofiller. From a practical standpoint, this copolyester shows far greater toughness than any styrenic, promising much more robust parts in the context of 3D printing, and nanocomposites based on copolysters of this type have exhibited enhances in stiffness and strength without losing their ductility or impact resistance (Beall et al, 2007; Jafferji et al, 2012).

In covering this work, we will demonstrate the general applicability of automated spray deposition as a means of additive manufacturing of polymeric materials through its successful application to the formation of two analogous families of nanolaminates, both based on high-$T_g$ amorphous thermoplastics with potential relevance to 3D printing. We will additionally report on the dynamic mechanical behavior of these systems as a function of nanofiller content and polymer-nanofiller interaction strength, using the latest data from our ongoing efforts to study copolyester nanolaminates to make preliminary comparisons in this context. In addition to providing a new means of accomplishing additive manufacturing, these efforts have clear implications for materials performance in the context of the 3D printing of polymer nanocomposites.

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REFERENCES


