

TECHNOLOGY ADVANCES

Precision Multilayer Technology Pushes Performance of High-Energy-Density Capacitors

Precision thin-film multilayer technology is being applied by researchers at Lawrence Livermore National Laboratory (LLNL) to push the performance limits of high-energy-density capacitors to new levels. At present, 0.5–1.0 J/cm³ prototype capacitors, 1 mm thick with a 4-cm² footprint, have achieved 50 J/cm³ dielectric energy densities. The goal of the work is to produce high-energy capacitors in the

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~100 J/cm³ range with increased energy density, a footprint of less than 1 cm², and a total height of less than 0.5 mm, as shown in Figure 1. Applications for the nanostructure multilayer capacitors (NMCs) include power electronics control circuitry, automotive control systems, telecommunications, and computers. In addition, such capacitors are found in most high-energy power supplies, radar systems, and pulsed radio-frequency applications. As snubber capacitors, they are used to protect power switching devices from voltage transients and to divert energy from a power device during switching transitions.

Nanostructure multilayers as a class of materials can be described as atomic-scale laminates comprising two to more than 200,000 layers. Each lamination varies in thickness from a few angstroms to several thousand angstroms and can be composed of a variety of materials. The researchers have fabricated multilayers out of 80 different elements. The multilayer fabrication method circumvents the standard method of tailoring atomic structure in the solid state, which relies on thermodynamics and kinetics to create the degree of order or disorder in

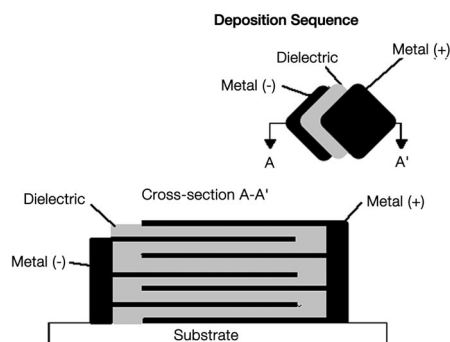


Figure 1. Idealized aspects of a multilayered capacitor design, showing the alternating metal and dielectric laminations and a cross section of the multilayered capacitor. The total height, including the substrate, will be less than 0.5 mm.

the structures. The structures are “atomically engineered,” a single layer of molecules or atoms at a time, using magnetron sputtering techniques. As a result of the precise chemical thickness and surface structure control, which transcends natural processes and standard manufacturing methods, surprising properties are detected in these nanolaminated multi-

layers, compared with the macro properties of the same materials. Each layer is only several atoms to several thousand atoms thick. As a result, the atoms within the layer are strongly influenced by both boundaries of the structure, creating what may be considered a new class of materials. The unexpected properties include increased hardness, increased strength, and resistance to corrosion and heat. Unexpected properties that are specific to the composition of the multilayers also have been identified.

Materials produced in this manner have found many applications, such as efficient reflecting structures in the x-ray, soft x-ray, and extreme-UV spectral domains. This, combined with other technological advances, has resulted in a renaissance in x-ray, soft x-ray, and extreme-UV physics, solar astrophysics, and short-wavelength technologies. Airbags and portable welding tools exemplify some of the breadth of this technology. Additional technologies, such as high-performance multilayer coatings for low-friction and low-wear applications, have been able to take

advantage of the unexpectedly high strength-to-weight ratio of these materials.

NMCs have been developed to scale high-energy-density capacitors to miniature proportions. Preliminary tests have indicated that these multilayered, high-energy-density, low-loss-tangent capacitors are rugged and have little to no capacitive voltage dependence. Current NMCs are composed of alternating sputter-deposited metallic and dielectric layers. Performance specifications (i.e., breakdown voltage, dielectric constant, and leakage current) are optimized by the appropriate selection of sputter-deposited dielectric materials. These are most commonly oxides of tantalum and niobium, Ta_2O_5 and Nb_2O_5 .

LLNL's patented reactive-sputtering process produces high-performance dielectrics with low microcontamination at high deposition rates. It is anticipated that the requirements for a high-volume commercialization facility will include at least a Class-1000 clean room and cluster tools with advanced heads made by physical vapor deposition. It is possible that a limited number of Class-100 clean-room pro-

duction facilities or self-contained automated cluster tools may also be required.

Opportunities

The patented capacitor technology is available for licensing, with some opportunities for research and development partnerships. The University of California is seeking the appropriate industrial partner or combination of partners to commercialize this technology. In this particular case, it is possible to envision the appropriate manufacturing facility partnering with a company that has present interest in or plans to expand into the area of high-energy-density capacitors.

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For licensing and partnership opportunities: Industrial Partnerships and Commercialization Office, Lawrence Livermore National Laboratory, PO Box 808, L-795, Livermore, CA 94551-0808, USA; tel. 925-422-6416 and e-mail capacitors@llnl.gov.

A Direct-Blending Approach for Polypropylene/Clay Nanocomposites Enhances Properties

The commercial importance of polypropylene (PP) has driven the investigation of PP composites reinforced by particulates, fibers, and layered inorganic fillers. Specifically, with respect to layered inorganic fillers, the aluminosilicate minerals talc and mica have been of greatest interest. However, recent advances in polymer/clay and polymer/silicate nanocomposite materials have motivated efforts to disperse fillers in PP based on montmorillonite, a naturally occurring mineral in the 2:1 aluminosilicate family. Because of PP's nonpolar (aliphatic) nature, it has proved challenging to develop a clay-based filler that is directly miscible with neat (i.e., nonfunctionalized) PP.

To date, most of the efforts that have shown some success employ a two-step process. First, a polymer/clay "master batch" is compounded, usually by mixing a functionalized (e.g., maleic anhydride) PP with high loadings of alkyl-ammonium-modified montmorillonite. This "master batch" is subsequently blended with neat PP, usually assisted by strong mechanical shear in an extruder or mixer. In this manner, the PP polymer and the master batch are effectively at θ conditions (i.e., the energy of the mixture is the same as the

energy of the separate components), and the extrusion is only promoting mixing of the clay in the neat-PP matrix due to the effect of the mechanical shear. As a result, the structure and the properties of the hybrid material produced depend strongly on the processing conditions and range from moderate dispersions and modest property improvements to good dispersions and better performing hybrids. It is still under investigation whether the clay dispersion in these structures is amenable to further processing or whether the fillers reaggregate.

The resulting PP/inorganic hybrids produced by this two-step process typically have enhanced modulus and barrier properties, but poor thermal and impact

behaviors. Even more important, reliability suffers in that hybrids with consistent properties are not formed even when the same materials and processing conditions are used. This is not surprising, since the filler dispersion in the PP matrix is achieved by a process that traps the separate inorganic layers.

At The Pennsylvania State University, researchers have developed an alternate route of nanocomposite formation that uses a carefully selected semi-fluorinated organic surfactant to modify the montmorillonite clays. They use favorable mixing thermodynamics to promote and stabilize the clay dispersion in neat PP. Some representative materials properties are given in Table I.

The mechanical response is compara-

Table I: Typical Materials Properties for Polypropylene (PP)/Clay Nanocomposites Formed by Direct Blending of PP with Fluoro-Organic-Modified Montmorillonite (f-mmt)

Properties	Neat PP	PP/f-mmt Nanocomposites	
		3-wt% f-mmt	6-wt% f-mmt
Mechanical Properties			
Young's (tensile) modulus (MPa)	665.8	906.9	959.3
Yield stress (MPa)	28.9	31.3	30.6
Strain at break (%)	744.6	646.9	716.5
Other Properties			
Heat-deflection temperature (°C)	109	144	152
Max. heat-release rate (kW m ⁻²)	1508	452	390
Light transmittance (at $\lambda = 600$ nm)	0.58	0.57	0.49

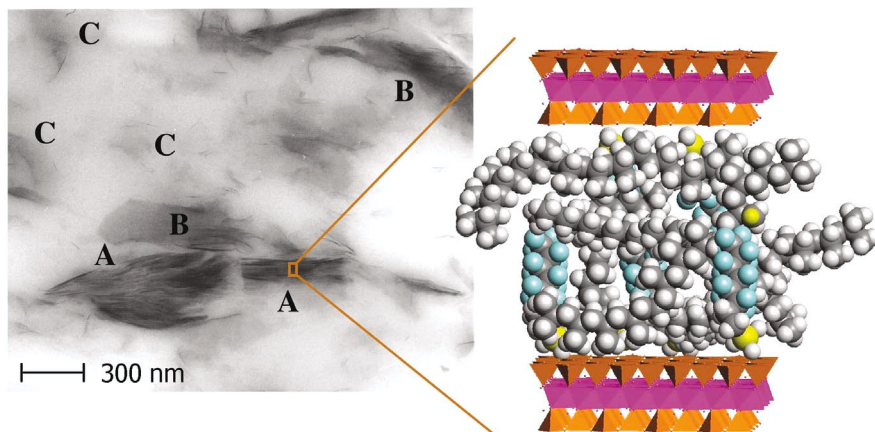


Figure 1. Bright-field transmission electron micrograph of the polypropylene (PP)/clay structure; black lines correspond to the clay layers and gray regions to the PP matrix. Note the coexistence of (A) intercalated (parallel-stacked and separated by 2–3 nm of PP) and (B) disordered (with comparable PP separations, but without parallel registry) tactoids—bunches of clay layers—with (C) exfoliated formations of 1–3 clay layers (separated by tens of nanometers of polymer). A, B, and C refer to the way that the dark lines (clay layers) are dispersed in the gray background (polymer).

ble with that of PP/clay hybrids formed by the “master batch” process; namely, an increased (by 150–200%) Young’s (tensile) modulus is the best that can be achieved without sacrificing the yield stress and the elongation at break. However, in the case of the fluoro-organic-modified montmorillonite-based (f-mmt) nanocomposites, there is also a notable elevation (by 35–43°C) of the *heat-deflection temperature* (i.e., the temperature at which a standard plastic test bar deflects a specified amount under an established load, per ASTM) and no marked loss of clarity in the visible wavelengths. Also, the barrier properties are improved, with water-vapor and oxygen permeabilities reduced by one-half at a 4-wt% f-mmt level. Clay dispersion also promotes flame-retardant properties, a characteristic common to almost all PP/clay hybrids independent of their preparation and structure. This last property enhancement arises from a surface char formation, which is thermally insulating and thus retards further combustion. The char layer is also highly impermeable to gases and fumes.

Beyond the improvement in properties, one of the most important features of the PP/f-mmt hybrids is that the clay dispersion (see Figure 1) is achieved independently of the conditions employed for the nanocomposite formation. This implies that the properties arising from the nanocomposite structure are maintained. For example, the improvement in heat-deflection temperature shown in Table I remains almost unchanged for direct PP/f-mmt blending by static melt intercalation, extrusion, solvent-assisted dispersion, and compression molding. Moreover, the

nanometer filler dispersion is maintained after subsequent processing, even at high temperatures and high shear rates; this has been verified under extrusion, mixing in an industrial mixer (Brabender), and cyclic compression-molding of the nanocomposite. This stability of the filler dispersion under further processing is expected, since the dispersion is determined by the thermodynamics of the system, in contrast with the trapping mechanism of the two-step process.

The researchers are currently exploring general design principles to concurrently enhance selected properties. They have developed a scheme (based on the extent of the surfactant fluorination) that allows for controlling the clay dispersion from mostly intercalated to almost fully exfoliated. This control becomes important when impact properties are considered, since exfoliation promotes Young’s modulus enhancement at the expense of impact strength, whereas intercalated structures promote impact strength. Thus, a mixed intercalated/exfoliated structure can be used to achieve a balance of high modulus and impact. Preliminary work suggests that the ability to control the clay dispersion would allow tailoring this balance at will.

Opportunities

Penn State is interested in establishing relationships with industrial partners to aid in the commercialization of this technology.

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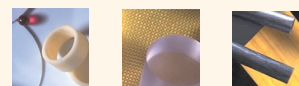


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