

Ethylene vinyl acetate properties improved with layered hybrid nanofillers

Prashant S. Khobragade, Dharmesh P. Hansora, Jitendra B. Naik, James Njuguna, and Satyendra Mishra

Addition of exfoliated magnesium-aluminum-layered double hydroxide/graphene oxide nanostructures, up to a loading of 0.7wt%, gives rise to significantly enhanced mechanical and thermal characteristics.

Ethylene vinyl acetate (EVA) is rapidly emerging as an alternative to traditional polymeric materials because of its desirable characteristics (e.g., softness, good mechanical and physical properties, easy processibility, and strong resistance to chemicals). EVA is also highly flexible, resistant to rupture, and exhibits excellent adhesion to a wide range of substrates. This elastomeric copolymer thus finds many different applications (depending on the vinyl acetate content) in several technical sectors.¹ EVA copolymers, however, are thermally unstable and burn rapidly, which limits their use in thermally elevated applications.

To make EVA copolymers usable in thermally sensitive situations, it is possible to add a variety of different filler materials (e.g., calcium carbonate,^{2–6} carbon nanotubes,⁷ and nanoclay^{8,9} nanofillers).¹⁰ Indeed, improving the physicochemical (i.e., thermal, mechanical, and physical) properties of EVA in this way has become a popular topic in recent times,¹¹ and EVA composites are now used as high-performance materials for insulating materials, hot melt adhesives, food packaging,¹² biomedical devices,¹³ as well as in construction, lubricants, transport, and electrical engineering applications. The high loading (3–4wt%) of inorganic nanofillers that is necessary to achieve the physicochemical improvements, however, can substantially increase the cost of the composites, and more cost-effective solutions are therefore required.

In this work,¹⁴ we have thus investigated the use of novel, cost-effective layered hybrid nanostructures as fillers to improve the physicochemical properties of EVA polymers. Our highly exfoliated layered nanostructures—LDH@GOs—consist of exfoliated graphene oxide (GO) and magnesium-aluminum-layered double hydroxides (LDHs), and were designed to produce multifunctional polymer nanocomposites.^{14,15} It is our overall aim to use the LDH@GO

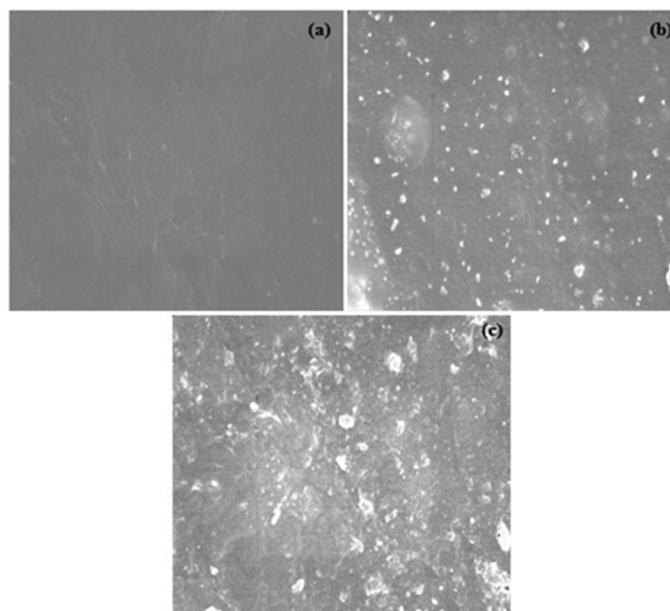


Figure 1. Field-emission scanning electron microscope images of the (a) neat ethylene vinyl acetate (EVA) sample and the EVA nanocomposite samples containing (b) 0.7wt% and (c) 1wt% of the exfoliated magnesium-aluminum-layered double hydroxide/graphene oxide (LDH@GO) nanostructures.

nanostructures in the development of materials that will be suitable for application in the aerospace, electronics, automotive, and construction industries.

To prepare our LDH@GO layered hybrid nanostructures, we used a one-pot microwave-assisted synthesis approach. In addition, our nanocomposite fabrication process involved two steps. In the first—solution reflux—step, we dissolved the desired amount of EVA in toluene. To obtain different nanocomposite compositions, we then added the LDH@GO-based layered hybrid nanostructures to the EVA

Continued on next page

Table 1. Differential scanning calorimetry and thermogravimetric analysis results for the EVA/LDH@GO hybrid nanocomposites. T_g : Glass transition temperature. T_m : Melting temperature. d_{on1} : First degradation step. d_{on2} : Second degradation step. d_{off} : Degradation offset temperature. W_L : Weight loss.

LDH@GO content (wt%)	T_g (°C)	T_m (°C)	d_{on1} (°C)	d_{on2} (°C)	d_{off} (°C)	W_L (%)
0.0	48 (±1)	83 (±1)	275 (±5)	395 (±5)	485 (±5)	99.12 (±1)
0.3	50 (±1)	86 (±1)	280 (±5)	400 (±5)	475 (±5)	98.85 (±1)
0.5	51 (±1)	88 (±1)	285 (±5)	405 (±5)	480 (±5)	98.52 (±1)
0.7	62 (±1)	91 (±1)	310 (±5)	440 (±5)	480 (±5)	97.32 (±1)
0.9	64 (±1)	89 (±1)	255 (±5)	405 (±5)	460 (±5)	98.50 (±1)
1.0	40 (±1)	86 (±1)	230 (±5)	400 (±5)	460 (±5)	98.23 (±1)

solution in concentrations of 0.3, 0.5, 0.7, 0.9, or 1wt%. While constantly stirring the EVA/LDH@GO solution, we increased the temperature up to 140°C and performed the reflux for 20 hours at this temperature. To achieve exfoliation, we performed vigorous stirring and increased the rate at which the layered hybrid materials were mixed into the EVA matrix. In the second step of our fabrication process, we cast and dried the composite solution at room temperature for five days, and then in a vacuum oven for 24 hours at 75°C. We then fed the mixed composite materials into an injection molding machine so that we could prepare dumbbell-shaped specimens for testing.

To investigate the effect of the LDH@GO nanostructures on EVA polymers, we performed complete characterizations of the samples' morphological, mechanical, and thermal properties. For example, we present (see Figure 1) the field-emission scanning electron microscope images we obtained for a cryogenically fractured neat EVA sample, and

samples that contained LDH@GO at loadings of 0.7 and 1wt%. The 0.7wt% LDH@GO image—see Figure 1(b)—reveals the exfoliated nature of the EVA matrix. In contrast—see Figure 1(c)—we observe partial aggregates or intercalated platelets in the 1wt% EVA/LDH@GO nanocomposite.

To determine the mechanical and thermal properties of the EVA and EVA/LDH@GO nanocomposites, we measured the tensile strength (TS) and elongation at break (EB) of the samples (see Figure 2). We find that the 0.7wt% LDH@GO nanocomposite exhibits the highest TS value (21MPa). This arises because of proper exfoliation, and because of the uniform dispersion of the layered hybrid nanostructures within the matrix (i.e., causing intermolecular interactions between the nanostructures and the matrix that enhance the elongation and increase the TS). Furthermore, we find that the EB of all the nanocomposites was higher than for the neat EVA sample. For example, we measured EB values of 105, 100, 114, and 150% for the 0.5, 0.7, 0.9, and 1wt% LDH@GO samples, respectively.

Our differential scanning calorimetry and thermogravimetric analysis (TGA) results are given in Table 1. We find that the glass transition temperature (T_g) and the melting temperature (T_m) of the EVA/LDH@GO hybrid nanocomposites were greater than those of the neat EVA sample. Although the T_g and T_m of the nanocomposites generally increase with increasing LDH@GO content, we do observe a slight decrease for the 0.9 and 1wt% samples. From the TGA, we measured the first degradation (d_{on1}) in the 275–310°C range and the second degradation (d_{on2}) in the 395–440°C range (we attribute these two steps to the evolution of acetic acid and to the degradation of ethylene-based chains in the EVA, respectively). Our results also indicate that the d_{on1} and d_{on2} of the EVA/LDH@GO hybrid nanocomposites increased with increasing filler loading (up to 0.7wt%).

In summary, we have examined the use of our novel LDH@GO layered hybrid nanostructures as fillers for an EVA copolymer matrix. In particular, we find that the addition of the exfoliated nanostructures, up

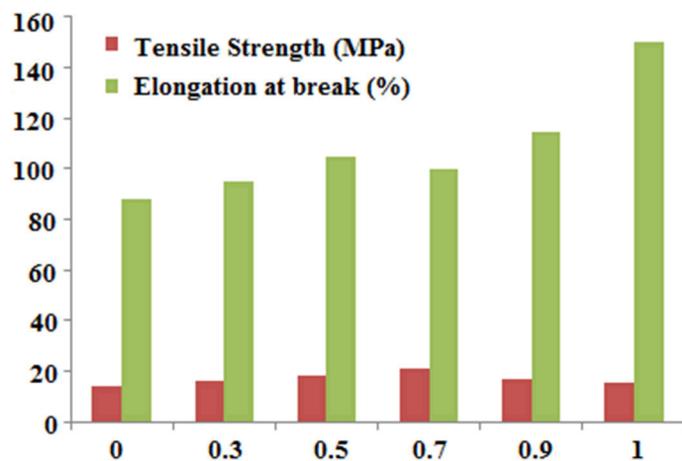


Figure 2. Tensile strength and elongation at break measurements for the neat EVA and EVA hybrid nanocomposites (containing 0.3, 0.5, 0.7, 0.9, and 1wt% LDH@GO nanostructures).

to a loading of 0.7wt%, can lead to significant enhancement of the polymer's mechanical and thermal properties. At higher loadings, however, the LDH@GO nanostructures become intercalated and aggregated. We are now investigating the potential of these materials for several applications, e.g., for use in antimicrobial packaging.

Author Information

Prashant S. Khobragade, Dharmesh P. Hansora, Jitendra B. Naik, and Satyendra Mishra

University Institute of Chemical Technology
North Maharashtra University
Jalgaon, India

Prashant Khobragade is a PhD student working under the guidance of Satyendra Mishra. His research is focused on the preparation, synthesis, and characterization of nanomaterials, hybrid nanomaterials, and nanocomposites.

Dharmesh Hansora was a researcher at the University Institute of Chemical Technology after he obtained his MTech from Maharaja Sayajirao University of Baroda, India. His research interests include polymer nanocomposites and their characterization.

Jitendra Naik is a professor and head of the Chemical Engineering Department. He obtained his PhD from North Maharashtra University, India, and his research interests include polymer composites, nanocomposites, and drug delivery.

Satyendra Mishra is a professor and director of the University Institute of Chemical Technology. His areas of research are wood polymer composites, polymer nanocomposites, biodegradable polymer composites, conducting polymer composites, and water-soluble polymers.

James Njuguna

School of Engineering
Robert Gordon University
Aberdeen, UK

James Njuguna is a reader of composite materials and structures, in the Centre for Advanced Engineering Materials, and is also the director of research. His research focuses on composite materials (and nanomaterials) for structural applications.

References

1. S. K. Suman, R. M. Kadam, R. K. Mondal, S. Murali, K. A. Dubey, Y. K. Bhardwaj, and V. Natarajan, *Melt-compounded composites of ethylene vinyl acetate with magnesium sulfate as flexible EPR dosimeters: mechanical properties, manufacturing process feasibility, and dosimetric characteristics*, **Appl. Radiat. Isotopes** **121**, pp. 82–86, 2017.
2. S. Mishra, N. G. Shimpi, and U. D. Patil, *Effect of Nano CaCO₃ on thermal properties of styrene butadiene rubber (SBR)*, **J. Polym. Res.** **14**, pp. 449–459, 2007.
3. S. Mishra, N. G. Shimpi, and A. D. Mali, *Investigation of photo-oxidative effect on morphology and degradation of mechanical and physical properties of nano CaCO₃ silicone rubber composites*, **Polym. Adv. Technol.** **23**, pp. 236–246, 2012.
4. S. Mishra and N. G. Shimpi, *Mechanical and flame-retarding properties of styrene-butadiene rubber filled with nano-CaCO₃ as a filler and linseed oil as an extender*, **J. Appl. Polym. Sci.** **98**, pp. 2563–2571, 2005.
5. S. Mishra and N. G. Shimpi, *Comparison of nano CaCO₃ and flyash filled with styrene butadiene rubber on mechanical and thermal properties*, **J. Sci. Indust. Res.** **64**, pp. 744–751, 2005.
6. S. Mishra, S. H. Sonawane, and R. P. Singh, *Studies on characterization of nano CaCO₃ prepared by the in situ deposition technique and its application in PP-nano CaCO₃ composites*, **J. Polym. Sci. Part B Polym. Phys.** **43**, pp. 107–113, 2005.
7. G. Sui, W. H. Zhong, X. P. Yang, Y. H. Yu, and S. H. Zhao, *Preparation and properties of natural rubber composites reinforced with pretreated carbon nanotubes*, **Polym. Adv. Technol.** **19**, pp. 1543–1549, 2008.
8. I. Ghasemi, M. Karrabi, M. Mohammadi, and H. Azizi, *Evaluating the effect of processing conditions and organoclay content on the properties of styrene-butadiene rubber/organoclay nanocomposites by response surface methodology*, **eXPRESS Polym. Lett.** **4**, pp. 62–70, 2010.
9. S. Mishra, N. G. Shimpi, and A. D. Mali, *Surface modification of montmorillonite (MMT) using column chromatography technique and its application in silicone rubber nanocomposites*, **Macromol. Res.** **20**, pp. 44–50, 2012.
10. R. El Hage, A. Viretto, R. Sonnier, L. Ferry, and J.-M. Lopez-Cuesta, *Flame retardancy of ethylene vinyl acetate (EVA) using new aluminum-based fillers*, **Polym. Degrad. Stabil.** **108**, pp. 56–67, 2014.
11. S. Mishra, S. Sonawane, and V. Chitodkar, *Comparative study on improvement in mechanical and flame retarding properties of epoxy-CaCO₃ nano and commercial composites*, **Polym.-Plast. Technol. Eng.** **44**, pp. 463–473, 2005.
12. A. Sonia and K. P. Dasan, *Celluloses microfibers (CMF)/poly (ethylene-co-vinyl acetate) (EVA) composites for food packaging applications: a study based on barrier and biodegradation behavior*, **J. Food Eng.** **118**, pp. 78–89, 2013.
13. N. Pramanik, S. Mohapatra, P. Bhargava, and P. Pramanik, *Chemical synthesis and characterization of hydroxyapatite (HAp)-poly (ethylene co vinyl alcohol) (EVA) nanocomposite using a phosphonic acid coupling agent for orthopedic applications*, **Mater. Sci. Eng. C** **29**, pp. 228–236, 2009.
14. P. S. Khobragade, D. P. Hansora, J. B. Naik, J. Njuguna, and S. Mishra, *Effect of multi-layered nanostructures on the physico-mechanical properties of ethylene vinyl acetate-based hybrid nanocomposites*, **Polym. Compos.**, 2017. doi:10.1002/pc.24371
15. P. S. Khobragade, D. P. Hansora, J. B. Naik, J. Njuguna, and S. Mishra, *Preparation and analysis of multi-layered hybrid nanostructures*, **Appl. Clay Sci.** **132–133**, pp. 668–674, 2016.