ENGINEERING

Nanocavities Double the Toughness of Graphene– Polycarbonate Composite^{**}

By Wei Ming Huang, Wei Fu Sun, Guo Hua Chen* and Li Tan*

Polymer nanocomposites filled with two or more carbon nanomaterials are of considerable interests and have attracted much attention due to the synergistic effect of those fillers.^[1–9] While electrical, thermal, or tensile properties of these nanocomposites have been studied and improved significantly, impact properties, generally referred as toughness, have received much less progress. It is known that toughness of a nanocomposite is dependent on the materials' capability in energy absorption or dissipation once an impact is given by an external load.^[4,10-14] Such an energy dissipation process is influenced by many factors, including the size and type of the filler,^[15–18] the intertwining of the macromolecular chains,^[19] the adhesion between the filler and the polymer matrix,^[20–23] and many others. Balancing all these factors to promote a tougher material is, however, not easy. For instance, many reported polymer nanocomposites with a single filler exhibited even lower toughness than the polymer matrix,^[24-28] with others showing increased values.^[15,29-31] Shin et al.^[4] suggested that, to have a tougher polymer fiber, the formation of an interconnected network of all the elements inside the composite was necessary. Lin et al.^[12] revealed that higher toughness could be obtained after the formation of large plastic deformation zones inside the calcium carbonate/ polypropylene (PP) composite. Wang et al.^[14] prepared PP/ ethylene-propylene-diene monomer (EPDM) blends to

control the rubber particle orientation in the PP matrix. When impact toughnesses along three fracture directions were measured, their values greatly varied versus the orientations of the rubber particle. Moreover, molecular dynamics (MD) simulations from Gersappe^[31] revealed that the ability to dissipate energy can be strengthened from the mobility of embedded fillers under applied stresses, supported by parallel reports from Shah *et al.*^[32] and Zhou *et al.*^[33] Hitherto, carbon-based nanomaterials such as graphene^[4,13,18] and carbon black (CB)^[27] have been used to reinforce polymer composites, with particular emphasis on toughness in terms of crack deflection, filler-matrix debonding, and energyconsuming polymer deformation. While interesting and inspiring, many of these studies failed to increase toughness of polycarbonate (PC). Mainly, PC has much different rheological behaviors. For example, PC flows rather easily above 300 °C, but a slight temperature drop below that will increase the viscosity substantially, limiting the dispersion of fillers, the network formation, as well as viable approaches to control adhesions between the filler and the polymer matrix.

In this work, we report the very first example of promoting toughness of PC with a completely different mechanism, that is, the formation of nanocavities. Instead of using sophisticated lithography or assembly techniques, our success is built on a thermal processing enabled nanofeature growth in bulk polymer, suggesting great ease in transplanting this mechanism to many other structural materials. Our proof-of-concept examples include a series of PC nanocomposites with two carbon-based fillers, namely, they are CB nanoparticles and graphene nanoplatelets (GNP). We either couple one of these fillers with PC or use both of them at the same time. We found that compounding CB and PC at 300 °C can trigger a nontrivial air expansion inside the porous CB nanoparticles, resulting in many cavity-wrapped particulates (sketches in Figure 1). In contrast, when GNP and CB were used together, GNP showed a unique capability in peeling the air sheath from the particulates, giving rise to nanocavities everywhere (Figure 1) and a significantly enhanced toughness (i.e., 100%). Benefited from these small pores, the carbon-based fillers found much ease in forming conducting paths, delivering two to three orders of magnitude leap in electrical conductivities.

We started our processes by dispersing the fillers into the PC matrix using a twin screw extruder, followed by injecting the resulted granules into an injection mold to form dumbbell-

1

^[*] Prof. G. H. Chen, W. M. Huang Department of Polymer Science and Engineering, Huaqiao University, Xiamen 361021, China E-mail: hdcgh@hqu.edu.cn Dr. W. F. Sun School of Materials Science asnd Engineering, University of New South Wales, Sydney, NSW 2052, Australia Prof. L. Tan Department of Mechanical and Materials Engineering, University of Nebraska, Lincoln, NE 68588, USA E-mail: ltan4@unl.edu

^[**] G. H. C. acknowledges the support from Natural Science Foundation of China (no. 51373059) and Science Foundation of Fujian Province (2013H6014). L. T. thanks the financial support from the National Science Foundation (CMMI-1068952 and IIA-1338988), the Nebraska Research Initiative, and the Min River fellowship from Fujian Province. Supporting Information is available from the Wiley Online Library or from the author.





Fig. 1. Schematic diagram of graphene promoting the formation of standalone nanocavities in polycarbonate (PC), where carbon black (CB) nanoparticles were responsible for the air expansion inside the polymer matrix.

or rectangle-shaped bars for toughness and other mechanical tests (See Experimental section for details). Figure 2a shows the Charpy V-notch toughness data of our PC composites with

GNP, CB, or GNP–CB. The measured toughness of our pure PC (\sim 15 kJ m⁻²) is consistent with reported results elsewhere (14–18 kJ m⁻²),^[34,35] the toughness of the nanocomposites with CB or GNP alone, i.e., 12–13 kJ m⁻², is slightly lower than but still comparable to that of the pure PC, a phenomenon not unusual if the inorganic particles acted as stress concentrators.^[27,28] Surprisingly, the toughness of the ternary composites loaded with two carbon-based fillers (\sim 23 kJ m⁻²) is almost twice that of those binary ones or more than 50% higher than pristine PC.

Figure 2b-e shows the scanning electron microscopy (SEM) images of the fractured nanocomposites. When CB or GNP was added into PC alone, all the fractured samples revealed smooth and clean wounds (Figure 2b and c), suggesting a rapid crack propagation during the impact test.[14,36-38] Certainly, this backs up our prior finding of lower toughness in composites with a single carbon-based filler and is also in good agreement with other reported findings.^[27,28] On the contrary, quite rough surfaces with sheet-like fragments were observed in ternary composites where both fillers of CB and GNP were added (Figure 2d and e, high magnification images in Figure 2h and i), implying intensive plastic deformations during the Vnotch impact. Not surprisingly, the incorporation of GNP alone does not produce any cavities inside the nanocomposites except occasionally protruded flakes or platelets (Figure 2f).^[23] On the other hand, adding CB alone introduced a small amount of cavities

(Figure 2g), suggesting a poor compatibility between CB and PC (Figure 2g and 3a–c). Different from those single filler composites, the incorporation of two carbon-based fillers at the same time produced a large amount of uniform nanocavities everywhere (Figure 2h, i, and 3d–f).

What should hold the responsibility for those nanosized pores or cavities? Recently, both Thio *et al.*^[23] and Lin *et al.*^[12] independently discovered that debonding along particlematrix interfaces can induce cavitations. Different from their pores of a few microns, our cavities are two orders of magnitude smaller in size and no obvious debonding-related marks are identified. In addition, the borders of our cavities carry an arc-like shape, suggesting the mechanism of debonding is not a major reason. Alternatively, people would think heat-induced mass loss could be a plausible reason, but our verdict is otherwise. Our thermogravimetric analysis (TGA) data (see Supporting Information, Figure S1) indicate no mass loss when the binary mixture was heated from 40 to 300° C. Here, the TGA results were tested in N₂ atmosphere while the composite processing was done in airtight



Fig. 2. (a) The impact properties of PC and PC composites utilizing graphene (GNP), CB, and GNP–CB, the total filler loading is kept at 1.0 wt%. (b–i) Scanning electron microscopy (SEM) images of the fractured composites: (b and f) GNP–PC, (c and g) CB–PC, (d and h) GNP/CB–PC (GNP/CB = 9:1), and (e and i) GNP/CB–PC (GNP/CB = 2:3).



condition. At the very beginning of the charging or feeding process, a small amount of air may be prone to be introduced. However, the in-flowing air may be inhibited and even expelled out due to the high pressure arisen from high temperature of charging barrel, although the possibility cannot be completely ruled out of. A close-up view of the nanocavities in Figure 3 reveals the sizes of those pores vary at different filler loadings/compositions. When CB was added alone, individual CB grain was always found with a thin sheath of air, where the thickness is in the order of 3 nm; when more CB was loaded, these particles would coalesce into large piles of aggregates, giving us cavities with a diameter of several hundred nanometers (Figure 3a-c). In contrast, when GNP was introduced with CB together, the thin sheath that was wrapping the CB solids would be pulled away, resulting in many uniform nanocavities, with almost all of them of a single size ($d \approx 45$ nm, Figure 3d–f). Seemingly, the introduction of GNP has changed the adhesion of CB nanoparticles.

Our first hypothesis is that the air expansion in porous CB particles has lead to the formation of those cavities. Most likely, during the high-temperature extruding and injection molding processes, the air temperature inside the particles has leaped from 298 K (25 °C) to 573 K (300 °C). Using the equation of the ideal gas law (PV = nRT), such a change will double the



Fig. 3. SEM images of nanocavities with CB particles in (a-c) CB–PC and (d-f) GNP/ CB–PC (GNP/CB = 2:3) composites, the total filler loading is kept at 1.0 wt%.

air volume or cause the trapped air to escape from those CB particles. If we assume the particles are spherical, given that their average diameter of 35 nm and a volume porosity of 60% (Evonik Degussa, Inc.), the trapped air in one of these tiny spheres ($V = 1.3 \times 10^4$ nm³) shall expand into an air balloon with an approximate diameter of 30 nm, in close proximity to those observed in Figure 3d-f. As a consequence, such an air balloon can exist as a thin sheath wrapping around the solid particle, forming a center-filled nanocavity with a diameter of 41 nm. However, all of these are not possible if PC flows easily back into the air-comprised sheath. In fact, this hypothesis is valid only because of the unusual rheological behavior of PC. Different from many thermoplastics, PC has a large entanglement density or large numbers of entanglement point per unit volume. Such a noncovalent but extensive network renders the polymer a low viscosity only after a high temperature (ca. \geq 240 °C). In our compounding process, right after the air expanded at 300 °C, the extruding temperature was lowered to slightly below 240 °C, resulting in a sharp increase in the viscosity of PC. Therefore, polymer chains have little chance to reorient, flow, or seal the newly formed cavities.

While the complex interplay of air expansion and entanglement of PC chains can explain the nanocavity growth process, it is still surprising to see the separation of those air sheaths from CB surfaces after the GNP incorporation. This prompted us with our second hypothesis, where we believe a closer interaction between CB and GNP has separated CB from the air balloons, manifesting the balloons as solid-free nanocavities^[39] as sketched in Figure 1. Our MD simulations (Figure 4) supported this hypothesis by comparing interaction energies between paired elements. To mimic the compounding processes, we allowed a certain gap between the elements before a mixing (Figure 4a). After a CB particle was placed next to GNP, we saw an ever-reducing gap between the two elements (Figure 4b-d). In contrast, when the PC chains were allowed to approach the CB (Figure 4c-f), their gap has never completely been removed (Figure 4g and h). To translate these compatibility differences^[40] using energy reduction as a parameter, we define an interaction energy (ΔE), i.e., $\Delta E = E_{AB} - (E_A + E_B)$, where E_A , E_B , E_{AB} are the potential energies of the component A, the component B, and the mixture of A and B, respectively. If we split the entire interaction as van der Waals (attraction) and the short-range repulsion (Born repulsion), we can calculate the ΔE as shown in Table 1. It is clear that the total interaction between CB particles and GNP or that between CB and PC is attractive, but the total energy reduction for the former (i.e., -146.21 ± 10.37 $kcalmol^{-1}$) is much greater than the latter combination $(-57.97 \pm 1.67 \text{ kcal mol}^{-1})$. Moreover, the total force acting on carbon nanoparticles along the z-axis can be evaluated by considering all possible forces exerted from GNP and PC chains.^[41] We managed to analyze five frames of equilibrated structures of the ternary components and received a negative value, i.e., -0.0473 ± 0.01 nN. (Note the positive sign of force corresponds to the positive direction of z-axis.) In other

3







Fig. 4. Sequential snapshots of mixing CB, GNP, and PC at the following times (side view): (a) 0 ps, (b) 50 ps, (c) 100 ps, (d) 150 ps, (e) 200 ps, (f) 250 ps, (g) 375 ps, and (h) 500 ps. The colors of cyan, red, and white represent carbon, oxygen, and hydrogen atoms, respectively.

words, this confirmed us a stronger interaction between the CB and GNP.

So far, we explained the nanocavity formation process in graphene-PC nanocomposites, what about the influence of these cavities to other mechanical properties such as elastic modulus, strength, and hardness? If we fix the filler loading to 1 wt%, our experimental results showed that the tensile strength of having hybrid fillers for composites (about 56 MPa) is roughly the same as that of a pristine PC or PC with a single filler (see Supporting Information, Figure S2a).

Table 1. Calculated interaction energies between different components $(kcal mol^{-1}).$

Mixture	Attraction-induced	Repulsion-induced	Interaction
	energy	energy	energy,
	reduction	gain	ΔΕ
$\begin{array}{c} CB+GNP\\ CB+PC \end{array}$	$-227.46 \pm 10.92 \\ -98.32 \pm 4.51$	$\begin{array}{c} 86.32 \pm 10.21 \\ 39.54 \pm 3.34 \end{array}$	$-146.21 \pm 10.37 \\ -57.97 \pm 1.67$

Likewise, the same trend can be found for hardness values (Figure S2b) or elastic modulus changes (Figure S2a). Simply, the incorporation of hybrid fillers in PC matrix enhanced the toughness without sacrificing the elastic modulus, the tensile strength, or the hardness.

When the loading of CB particulates was increased, extensive nanocavities could be found in CB-PC or CB-GNP-PC (see Supporting Information, Figure S3). While this trend agrees with both of our hypotheses above, abundance of small pores could collapse into micron-sized holes that can potentially degrade the composites. To our surprises, the incorporation of GNP never allowed that to happen; instead, cavities in the ternary composite kept their small sizes in the nanometer domains (see Supporting Information, Figure S3b). Beyond this discovery, we even saw two to three orders of magnitude leap in electrical conductivities (see Supporting Information, Figure S4), from 1.87×10^{-4} to $1.40 \times$ $10^{-1} \,\mathrm{S} \,\mathrm{cm}^{-1}$. This significant improvement can be ascribed to the fact that nanocavities herein are more or less equivalent to crystalline regions, compacting CB nanoparticles with GNP.

In summary, we reported an unusual phenomenon, where nanocavities can promote the toughness of graphene-PC composite, concurring with an increase in elastic modulus without sacrifice in strength or hardness. Graphene-incorporated polymers showed great performances in several categories, including electrical conduction, thermal con-

duction, and tensile resisting. Much less success, however, was reported to promote the impact resistance or materials' capability to absorb or dissipate impact energies. This statement was held especially true for PC, one of the most important engineering materials from polymer industry. Due to the extensive entanglement of the rigid polymer chains, using carbon-based fillers to promote toughness usually meets with a quick failure. Our example above is the very first of promoting toughness of PC and graphene-PC with a novel mechanism, that is, the formation of nanocavities. Instead of using sophisticated lithography or assembly techniques, our progress is built on a thermal processing enabled nanofeature growth in bulk polymers, suggesting great ease in transplanting this mechanism to many other structural materials.

1. Experimental

1.1. Materials

The raw materials of GNP (KNG-180, diameter of 20-50 µm, thickness of less than 100 nm) were purchased from the



Knano Graphene Technology GmbH, China; CB was supplied by Evonik Degussa (Printex[®] XE2B), with dibutyl phthalate (DBP) adsorption value of 420 cm^2 (100 g)⁻¹, BET nitrogen surface area of more than $1000 \text{ m}^2 \text{ g}^{-1}$, and particle diameter of 35 nm; PC (2805) was purchased from Bayer Material Science, Germany, with MFR of 10 g (10 min)⁻¹.

1.2. Sample Preparations

Nanocomposites used in this study were prepared by melt extrusion with a corotating twin screw extruder (SHI-20, Nanjing, China). Filler added polymers were palletized and molded in bar specimen using an injection molder (SA900V, Ningbo, China). The dimensions of the impact specimen are 10 mm in thickness, 4 mm in width, 80 mm in length, and 2 mm in depth for the V-shaped notch. The dimensions of the tensile specimen are 4 mm in thickness, 10 mm in width, and 150 mm in length (50 mm was used to attach strain gauges). The samples for conductivity measurements were prepared as follows: first, CB nanoparticles were weighed and mixed with GNP at certain ratio, followed by feeding this hybrid with PC at room temperature. An internal mixer, operating at 300 °C and 90 rpm, was used for compounding the ternary mixtures. After being agitated for 15 min, the mixtures were removed and allowed to be cooled naturally to room temperature. Then, the resulting mixtures were loaded into a custom-made mold, followed by hot pressing to receive disk-shaped samples with a diameter of 25 mm and a thickness of 10-15 mm. Finally, the samples were polished using aluminum oxide waterproof abrasive papers (Shanghai, China) before the electrical test blow.

1.3. Spectroscopies

SEM images were taken with an S-4800 (II) FE-SEM (Hitachi, Japan). The samples were from the composite bars or disks, cut by a razor blade. Thermal gravimetric analysis (TGA) was carried out on a TG209 F3 (Netzsch, Germany) with a heating rate of $10 \,^{\circ}\text{C}\,\text{min}^{-1}$ under a nitrogen flow $(20 \,\text{L}\,\text{min}^{-1})$.

1.4. Electrical and Mechanical Tests

Conduction resistances were measured along the thickness direction. The composites' volume resistance that is less than $10^6 \Omega$ cm was measured using a SZ-82 four-point probe apparatus (Suzhou, China) and/or a DT9203A digital multimeter (Shenzhen, China). Composites with higher resistance (more than $10^6 \Omega$ cm) were measured with a ZC36 high resistivity meter (Shanghai, China) at room temperatures. Tensile tests were performed using CMT 6000 (SANS CO. Ltd., Shenzhen, China) at a constant strain rate of 2 mm min⁻¹ at room temperature. The notched Charpy impact toughness was measured with an impact test machine (ZBC-4, Shenzhen, China). The hardness of nanocomposites was evaluated with a QYS-96 plastic ball indentation machine (Changchun Intelligent Instrument CO. Ltd., China). Each final electrical or mechanical data was based upon data points of five different samples.

1.5. MD Simulation

See Supporting Information for details.

Received: March 22, 2014 Final Version: March 27, 2014 COMMUNICATION

- A. Yu, P. Ramesh, X. Sun, E. Bekyarove, M. E. Itkis, R. C. Haddon, *Adv. Mater.* 2008, 20, 4740.
- [2] D. Cai, M. Song, C. Xu, Adv. Mater. 2008, 20, 1706.
- [3] R. Wang, J. Sun, L. Gao, C. Xu, J. Zhang, Chem. Commun. 2011, 47, 8650.
- [4] M. K. Shin, B. Lee, S. H. Kim, J. A. Lee, G. M. Spinks, S. Gambhir, G. G. Wallace, M. E. Kozlov, R. H. Baughman, S. J. Kim, *Nat. Commun.* 2012, 3, 650.
- [5] Y. Pan, H. Bao, L. Li, ACS Appl. Mater. Interfaces 2011, 3, 4819.
- [6] M. Safdari, M. Al-Haik, Nanotechnology 2012, 23, 405202.
- [7] Y. Li, R. Umer, A. Isakovic, Y. A. Samad, L. Zheng, K. Liao, *RSC Adv.* 2013, *3*, 8849.
- [8] G. Zhang, J. Karger-Kocsis, J. Zou, Carbon 2010, 48, 4289.
- [9] S. Y. Yang, W. N. Lin, Y. L. Huang, H. W. Tien, J. Y. Wang, C. C. M. Ma, S. M. Li, Y. S. Wang, *Carbon* 2011, 49, 793.
- [10] T. Wang, C. H. Lei, D. Liu, M. Manea, J. M. Asua, C. Creton, A. B. Dalton, J. L. Keddie, *Adv. Mater.* 2008, 20, 90.
- [11] M. A. Rafiee, J. Rafiee, Z. Wang, H. Song, Z. Z. Yu, N. Koratkar, ACS Nano 2009, 3, 3884.
- [12] Y. Lin, H. Chen, C. M. Chan, J. Wu, *Macromolecules* 2008, 41, 9204.
- [13] L. S. Walker, V. R. Marotto, M. A. Rafiee, N. Koratkar, E. L. Corral, ACS Nano 2011, 5, 3182.
- [14] Y. Wang, Q. Zhang, B. Na, R. N. Du, Q. Fu, K. Z. Shen, *Polymer* 2003, 44, 4261.
- [15] Y. S. Thio, A. S. Argon, R. E. Cohen, M. Weinberg, *Polymer* 2002, 43, 3661.
- [16] W. C. J. Zuiderduin, C. Westzaan, J. Huetink, R. J. Gaymans, *Polymer* 2003, 44, 261.
- [17] K. Yang, Q. Yang, G. X. Li, Y. Zhang, P. Zhang, Polym. Eng. Sci. 2007, 47, 95.
- [18] C. Yu, Z. Chen, H. Li, J. Turner, X. Zeng, Z. Jin, J. Jiang,
 B. Youssef, L. Tan, *Adv. Mater.* 2010, 22, 4457.
- [19] R. Rafiq, D. Cai, J. Jin, M. Song, Carbon 2010, 48, 4309.
- [20] J. Jancar, A. T. Dibenedetto, A. Dianselmo, Polym. Eng. Sci. 1993, 33, 559.
- [21] G. J. Price, D. M. Ansari, Polym. Int. 2004, 53, 430.
- [22] T. Ahsan, D. A. Taylor, J. Adhes. 1998, 67, 69.
- [23] Y. S. Thio, A. S. Argon, R. E. Cohen, Polymer 2004, 45, 3139.
- [24] K. Wakabayashi, C. Pierre, D. A. Dikin, R. S. Ruoff, T. Ramanathan, L. C. Brinson, J. M. Torklson, *Macromolecules* 2008, 41, 1905.
- [25] K. Wakabayashi, P. J. Brunner, J. Masuda, S. A. Hewlett, J. M. Torkelson, *Polymer* 2010, *51*, 5525.
- [26] X. Jiang, L. T. Drzal, Polym. Compos. 2010, 31, 1091.

5



- [27] J. A. Manson, L. H. Sperling, Polymer Blends and Composites, Plenum Press, New York, USA 1976, p. 172.
- [28] I. Novák, I. Krupa, I. Janigova, Carbon 2005, 43, 841.
- [29] Z. Bartczak, A. S. Argon, R. E. Cohen, M. Weinberg, *Polymer* 1999, 40, 2347.
- [30] A. S. Argon, R. E. Cohen, Polymer 2003, 44, 6013.
- [31] D. Gersappe, Phys. Rev. Lett. 2002, 89, 301.
- [32] D. Shah, P. Maiti, D. D. Jiang, C. A. Batt, E. P. Giannelis, *Adv. Mater.* 2005, 17, 525.
- [33] T. H. Zhou, W. H. Ruan, M. Z. Rong, M. Q. Zhang, Y. L. Mai, Adv. Mater. 2007, 19, 2667.

- [34] S. S. Pesetskii, B. Jurkowski, V. N. Koval, J. Appl. Polym. Sci. 2002, 84, 1277.
- [35] A. K. Bledzki, H. Kirschling, J. Cell. Plast. 2004, 40, 489.
- [36] R. Gensler, C. J. G. Plummer, C. Grein, H. H. Kausch, *Polymer* **2000**, *41*, 3809.
- [37] J. Shi, Y. Wang, Y. Gao, H. Bai, Compos. Sci. Technol. 2008, 68, 1338.
- [38] T. Takayama, M. Todo, J. Mater. Sci. 2006, 41, 4989.
- [39] S. Neyertz, D. Brown, Macromolecules 2013, 46, 2433.
- [40] W. F. Sun, Q. H. Zeng, A. B. Yu, Langmuir 2013, 29, 2175.
- [41] W. F. Sun, Q. H. Zeng, A. B. Yu, K. Kendall, *Langmuir* 2013, 29, 7825.