Journal of Materials Chemistry A



View Article Online

View Journal | View Issue

PAPER



Cite this: J. Mater. Chem. A, 2015, 3, 21194

Nacre-inspired integrated nanocomposites with fire retardant properties by graphene oxide and montmorillonite[†]

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Natural nacre exhibits extraordinary strong and tough properties with its brick-and-mortar structure that was perfected after millions of years of evolution. Inspired by nacre's hierarchical structure, we fabricated multifunctional bioinspired nanocomposites of graphene oxide (GO) and montmorillonite (MMT) nanosheets with poly(vinyl alcohol) (PVA) *via* a vacuum-assisted filtration self-assembly process. By combining graphene oxide and montmorillonite with PVA, we demonstrated an effective synergistic toughening effect and obtained integrated strong and tough bioinspired nanocomposites. Furthermore, these nanocomposites show high fatigue-resistant properties, high electrical conductivity and good fire retardant properties. As such, they have promising potential in many applications, including flexible electrodes, flame retardant insulation and as aerospace materials. The technique developed here provides new insights for designing nanocomposites with a complex hierarchical structure that mimic nacre.

Received 26th July 2015 Accepted 15th September 2015

DOI: 10.1039/c5ta05742f

www.rsc.org/MaterialsA

1. Introduction

Due to its extraordinary mechanical and electrical properties, graphene shows promising applications in many fields.¹ However, assembling graphene nanosheets into macrosized bulk nanocomposites for these applications remains a great challenge.² Nacre, the gold standard for biomimicry, provides an excellent example and guidelines for assembling twodimensional (2D) nanosheets into high performance nanocomposites.³ The integrated strength and toughness of nacre are attributed to its brick-and-mortar structure with 95 vol% aragonite platelets and 5 vol% polymer including nanofibrillar chitin and proteins,⁴ and the refined interfacial interactions, which defuse the conflicts between strength and toughness.^{3,5} This unique hierarchical structure provides a new strategy for constructing ternary nanocomposites with integrated high strength and toughness through synergistic effects.^{6,7} For example, Prasad et al.8 reported the extraordinary synergistic effect in the ternary nanocomposites with two different nanocarbons incorporated into poly(vinyl alcohol) (PVA). Shin et al.9

demonstrated ultratough nanocomposite fibers through synergistic toughening of 2D graphene oxide (GO) and 1D singlewalled carbon nanotubes (SWNTs). Recently, we have demonstrated robust ternary nanocomposites through synergistic toughening in two systems: (1) montmorillonite (MMT)/nanofibrillar cellulose/PVA,⁶ and (2) GO/molybdenum disulfide (MoS₂)/thermoplastic polyurethanes (TPUs).⁷ The mechanical properties of ternary nanocomposites with effective synergistic toughening are superior to those of natural nacre and other binary layered nanocomposites. On the other hand, the MMT nanosheets, are also ideal candidates for constructing the multifunctional bioinspired nanocomposites,^{10–16} due to their excellent mechanical and fire retardant properties.

Herein, we advance our findings by describing the fabrication of integrated strong, tough and conductive ternary bioinspired nanocomposites with fire retardant properties based on graphene oxide (GO), montmorillonite (MMT) and poly(vinyl alcohol) (PVA) through synergistic effects emerging from building blocks and interfacial interactions. The tensile strength and tensile toughness of ternary bioinspired nanocomposites reach 356.0 MPa, and 7.5 MJ m^{-3} , which are 2- and 2.3-times higher than those of pure reduced GO films (a tensile strength of 178.1 MPa, and a tensile toughness of 3.3 MJ m⁻³), and are higher than those of most of the binary GO-based nanocomposites, respectively. Furthermore, these ternary bioinspired nanocomposites show high fatigue-resistant properties, high electrical conductivity of 136.4 S cm⁻¹, and good fire retardant properties. These multifunctional bioinspired nanocomposites show great potential applications in the fields of

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ta05742f

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aerospace, flexible electrodes, and flame retardant insulation. The technique developed here provides new insights for designing nanocomposites with a complex hierarchical structure that mimic nacre.

2. Results and discussion

2.1. Preparation process of bioinspired nanocomposites

The atomic force microscopy (AFM) images show the exfoliated GO and MMT nanosheets in Fig. S1.[†] The average diameter of GO and MMT nanosheets is about 1.2 µm, and 100 nm, respectively. The thickness of GO and MMT is about 0.75 nm and 1.2 nm, respectively, which is consistent with previous reports,10,17 indicating that exfoliated GO and MMT nanosheets are essentially monolayers. Before fabricating the GO-MMT-PVA ternary nanocomposites, the GO-MMT binary hybrid layered materials were assembled through vacuum-assisted filtration to optimize the ratio of GO to MMT. Six different weight ratios of GO to MMT (10:90, 30:70, 50:50, 70:30, 80: 20, and 90: 10) were chosen and the corresponding hybrid layered materials were designated as GO-MMT-I, GO-MMT-II, GO-MMT-III, GO-MMT-IV, GO-MMT-V, and GO-MMT-VI, respectively. The real mass percentages of the GO content were confirmed by thermogravimetric analysis (TGA), as shown in

Fig. S2 and Table S1.[†] SEM images of these binary layered materials show a typical nacre-like layered structure, as shown in Fig. S3.[†] The typical stress–strain curves and mechanical properties of GO–MMT binary hybrid layered materials are shown in Fig. S4 and Table S2.[†] Our results indicate that the tensile strength of binary GO–MMT hybrid layered materials reaches maximum when the GO content is about 90 wt%, which is consistent with other previous reports.^{18,19} Thus, we controlled the mass ratio of GO to MMT to be 90 : 10 for constructing the ternary bioinspired nanocomposites of GO–MMT–PVA in the following experiments.

The schematic illustration of the fabrication process of rGO-MMT-PVA ternary bioinspired nanocomposites is shown in Fig. 1a. The GO nanosheets were first dispersed into deionized water to obtain homogeneous solutions. Then, the MMT and PVA solution were added and ultrasonicated for 0.5 hour, respectively. After vacuum-assisted filtration, the ternary nanocomposites of GO-MMT-PVA were obtained. The rGO-MMT-PVA ternary bioinspired nanocomposites were achieved after chemical reduction with hydroiodic acid (HI) and washing with deionized water and ethyl alcohol,²⁰ respectively. The digital image of the resultant ternary bioinspired nanocomposites is shown in Fig. 1b, which shows a bit of metallic luster. To further demonstrate the effect of the PVA content on the mechanical



Fig. 1 Schematic illustration of the preparation process of the rGO–MMT–PVA ternary bioinspired nanocomposites through vacuum-assisted filtration self-assembly. (a) The GO, and MMT nanosheets were dispersed into deionized water by stirring and sonication. Then the PVA solution was added into the mixed solutions. After sonication, the uniform suspension was vacuum-assisted filtered into GO–MMT–PVA nano-composites. With HI reduction, the rGO–MMT–PVA ternary bioinspired nanocomposites were obtained. (b) Digital image of rGO–MMT–PVA ternary bioinspired nanocomposites were obtained. (b) Digital image of rGO–MMT–PVA ternary bioinspired nanocomposites were obtained. (c) SEM image of the cross-section of rGO–MMT–PVA. (d) Corresponding EDS of the Si element originating from MMT in rGO–MMT–PVA, revealing that MMT nanosheets are homogeneously distributed without aggregation. (e) The high resolution TEM image of the cross-section of rGO–MMT–PVA shows a well-ordered layered structure, which is further amplified in the blue scale section analysis in (f). (g) The complete element distribution of MMT is seen in the EDS spectrum, indicating the uniform dispersion of MMT in the resultant nanocomposites.

properties, five different weight ratios of the GO-MMT-PVA ternary nanocomposites with the same mass ratio of GO to MMT as 90 : 10 were prepared, including: GO-MM-PVA-I (GO : MMT : PVA = 45 : 5 : 50, GO-MMT-PVA-II (GO : MMT : PVA = 67.5 : 7.5 : 25), GO-MMT-PVA-III (GO : MMT : PVA = 76.5 : 8.5 : 15), GO-MMT-PVA-IV (GO : MMT : PVA = 81 : 9 : 10) and GO-MMT-PVA-V (GO : MMT : PVA = 85.5 : 9.5 : 5). The real mass percentages of the PVA content were confirmed by TGA, as shown in Fig. S5 and Table S3.† The cross-section morphology of rGO-MMT-PVA ternary bioinspired nanocomposites is a typical layered structure (Fig. 1c). Energy dispersive X-ray spectroscopy (EDS) was performed on this cross-section, and the result of EDS shows a uniform distribution of Si in Fig. 1d, indicating that the MMT nanosheets were uniformly dispersed in the resultant bioinspired nanocomposites.¹⁰ The crosssection morphology and EDS results of rGO-MMT-PVA ternary bioinspired nanocomposites with different PVA contents are shown in Fig. S6.[†] The cross-section of rGO-MMT-PVA nanocomposites shows a well-ordered layered structure, as shown in Fig. 1e and the amplified blue scale section of Fig. 1f. The complete element distribution of MMT is seen in the EDS spectrum, indicating the uniform dispersion of MMT in the resultant nanocomposites. In addition, X-ray diffraction (XRD) results further confirm the well-ordered intercalation of MMT into the interlamination of GO nanosheets, as shown in Fig. S7.[†] The *d*-spacing of GO–MMT–PVA nanocomposites is listed in Table S4,[†] which confirms that PVA is also uniformly distributed in the interlayer of the nanocomposites.

In fact, there are strong interfacial interactions between PVA, GO nanosheets, and MMT platelets.^{16,21} As mentioned in the previous report,²¹ the strong hydrogen bonding between the GO nanosheets and PVA chain increases the interfacial strength of the resultant nanocomposites, as shown in Fig. S8a.† Mean-while, the covalent bonding of Al–O–C between MMT and PVA further increases the interfacial strength.¹⁶ The corresponding characterization using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) spectra is shown in Fig. S8.† The positive energy shift of Al from 74.27 eV



Fig. 2 (a) Tensile stress–strain curves of the GO film (Curve 1), GO–MMT-VI (90 : 10) binary layered materials (Curve 2), rGO–MMT-VI layered materials (Curve 3), GO–MMT–PVA-IV nanocomposites (Curve 4), and rGO–MMT–PVA-IV ternary bioinspired nanocomposites (Curve 5). (b) and (c) The tensile strength and toughness of ternary bioinspired nanocomposites with different PVA contents, indicating that the optimal PVA content for the maximum tensile strength and toughness in ternary bioinspired nanocomposites is about 9.4 wt%. (d) Proposed synergistic mechanism of rGO–MMT–PVA ternary bioinspired nanocomposites. When stretching starts, the rGO nanosheets begin to slide and initiate the crack. With continuous stretching, the MMT platelet nanosheets bridge the crack and offer resistance to rGO nanosheet sliding, initiating the sliding sites of the adjacent rGO nanosheets. Finally, the ternary bioinspired nanocomposites fracture in the mode of rGO and MMT platelet pullout. (e) The fracture morphology of ternary bioinspired nanocomposites shows that the rGO nanosheets are pulled out. The inset is EDS of the Si element, indicating that much more friction between rGO nanosheets and MMT platelets occurred in the fracture process.

for pure MMT to 74.77 eV for MMT–PVA and 74.47 eV for GO– MMT–PVA, respectively, is indicative of the increased oxidation state of Al (Fig. S8b†).¹⁶ Meanwhile the change of ratios of carbon peaks at 284.4 eV (–C–H₂) and 285.9 eV (–C–O–H) observed in Fig. S8c† shows the covalent bonding of Al–PVA bonds in the MMT–PVA and GO–MMT–PVA. The FTIR spectra also confirm the Al–O–C covalent bonding at the characteristic vibration of 848 cm⁻¹ and the strong suppression of the C–O–H band at 3290 cm⁻¹ (Fig. S8d and e†), which is consistent with previous report.¹⁶

2.2. Mechanical properties and proposed crack mechanism

Typical stress-strain curves of pure GO films, GO-MMT-VI, rGO-MMT-VI binary layered materials, GO-MMT-PVA-IV, and rGO-MMT-PVA-IV nanocomposites are shown in Fig. 2a. The ternary bioinspired nanocomposites of rGO-MMT-PVA-IV show outstanding integration of strength and toughness of 356.0 \pm 15.5 MPa and 7.5 \pm 1.1 MJ m⁻³, respectively, which are 2- and 2.3-times higher than those of pure reduced GO films. The detailed mechanical properties of other ternary bioinspired nanocomposites are listed in Table S5.† For rGO-MMT-PVA ternary nanocomposites, the tensile strength and toughness reach the maximum value at the PVA content of about 9.4 wt%, as shown in Fig. 2b and c. When the PVA content is over 9.4 wt%, GO and MMT were fully wrapped by PVA, resulting in decreasing the energy transfer efficiency among GO, MMT nanosheets and PVA. On the other hand, when the PVA content is below 9.4 wt%, the cross-linking contains hydrogen and covalent bonding among GO, MMT and PVA is not enough, which cannot further increase the interfacial strength of the resultant nanocomposites.

To understand the synergistic strengthening effect from 2D GO nanosheets and MMT platelets, a crack extension model is proposed, as shown in Fig. 2d. When the rGO-MMT-PVA ternary bioinspired nanocomposites are subjected to stress, the hydrogen bonds are first destroyed, and the rGO nanosheets begin to slide over each other, initiating the crack. Then the friction between rGO nanosheets and MMT platelets leads to the movement of MMT along rGO nanosheets. With further

increase of the stress, the covalent bonds of Al–O–C between the MMT platelets and PVA molecular chain are damaged, and therefore, much more energy is absorbed. This cycling of crack initiation–propagation–deflection would continue until the rGO–MMT–PVA ternary bioinspired nanocomposites fracture, resulting in more energy being absorbed and therefore higher strength. The MMT and rGO nanosheets were pulled out and the corresponding fracture morphology is shown in Fig. 2e. The Si element (by EDS) was observed on the fractured surface of ternary bioinspired nanocomposites, indicating the sliding that existed between MMT platelets and rGO nanosheets. Other ternary bioinspired nanocomposites show a similar fracture morphology, including front and side views in Fig. S9.†

2.3. Synergistic effect from GO and MMT nanosheets

In order to quantify the synergistic effect of the mechanical properties' improvement, the synergy percentage (S) first proposed by Prasad⁸ is modified as follows:

$$S = \frac{2\sigma_{\rm hyb} - (\sigma_{\rm MMT} + \sigma_{\rm GO})}{\sigma_{\rm MMT} + \sigma_{\rm GO}} \times 100$$

where σ_{hyb} , σ_{MMT} , and σ_{GO} represent the mechanical properties of GO–MMT–PVA ternary nanocomposites, MMT–PVA and GO–PVA binary nanocomposites, respectively. The synergy percentage of tensile strength for MMT–PVA, GO–PVA, GO– MMT–PVA and rGO–MMT–PVA nanocomposites is also listed in Table S5.† As shown in Fig. S10,† the synergy percentage dramatically increases with GO contents. For example, the synergy percentage increases from 25.2% for rGO–MMT–PVA-I to 143.1% for rGO–MMT–PVA-IV. After that, the synergy percentage decreases. This may be ascribed to the fact that the cross-linking contains hydrogen and covalent bonding among GO, MMT and PVA is not enough at a low content of PVA to further increase the load transfer between GO and MMT nanosheets.

The ternary bioinspired nanocomposites were also fatigue tested in tension mode, as shown in Fig. S11(a-c).† The frequency of the loading tests was set to 1 Hz, and the stress ratio (*R*: minimum stress to maximum stress) was set to 0.1; the



Fig. 3 (a) Maximum stress (*S*) – number of cycles to failure (*N*) in tension mode for the ternary rGO–MMT–PVA bioinspired nanocomposites and the corresponding binary rGO–MMT nanocomposites. (b) Comparison of tensile strength and toughness of our ternary bioinspired nanocomposites, other GO-based layered materials, and natural nacre. The rGO–MMT–PVA ternary bioinspired nanocomposites show integrated high strength and toughness, which are superior to those of other GO-based nanocomposites with strong interfacial interactions, and weak interfacial interactions, such as hydrogen bonding and ionic bonding, respectively, and other ternary bioinspired nanocomposites of rGO–MOS₂–TPU.

S (the maximum stress)–*N* (the number of cycles to failure) curve is shown in Fig. 3a, and the corresponding cross-section SEM images are shown in Fig. S11(d–n);† the ternary rGO–MMT–PVA bioinspired nanocomposites show excellent fatigue properties compared with binary rGO–MMT nanocomposites. For instance, at the same stress level, the fatigue life of ternary rGO–MMT–PVA bioinspired nanocomposites is four orders of magnitude higher than that of binary rGO–MMT nanocomposites, due to the synergistic toughening effect from hydrogen and covalent bonding among GO, MMT and PVA. The high fatigue life of the ternary rGO–MMT–PVA bioinspired nanocomposites indicates their great potential applications in the fields of aerospace and flexible electrodes.

Compared with natural nacre⁴ and other GO-based binary nanocomposites,²² the ternary bioinspired nanocomposites show unique integrated tensile strength and toughness together (Fig. 3b), which are superior to those of other GO-based binary nanocomposites with strong interfacial interactions, such as covalent bonding of GO–GA,²³ GO–PAA,²⁴ GO–borate,²⁵ PGO– PEI,²⁶ rGO–PCDO,²⁷ and rGO–PDA,²⁰ weak interfacial interactions, such as hydrogen bonding of GO–CA²⁺,³¹ GO–Mg²⁺,³¹ and GO–Fe³⁺,³² and ternary rGO–MOS₂–TPU,⁷ respectively. The detailed mechanical properties of natural nacre, other GObased binary and ternary nanocomposites and our ternary bioinspired nanocomposites are listed in Table S6.[†]

2.4. Electrical properties of ternary bioinspired nanocomposites

Furthermore, our ternary bioinspired nanocomposites also show excellent electrical conductivity with a maximum of 136.4



Fig. 4 Ternary bioinspired nanocomposites act as a fire shield to protect a silk cocoon. (a) It took only 5 seconds to burn the silk cocoon. (b) The silk cocoon is well kept from burning for 5 minutes with rGO–MMT–PVA ternary bioinspired nanocomposites, which is exposed to an alcohol burner from the back side after the polymer PVA is removed. (c) and (d) SEM images of the ternary bioinspired nanocomposites after flame treatment, showing the tightly armored skin and mesoporously layered interior, similar to the previous report.

S cm⁻¹ for rGO–MMT–PVA-V, which is higher than that of previous ternary bioinspired nanocomposites of rGO–MoS₂– TPU⁷ and rGO–PVA binary nanocomposites.²⁹ As demonstrated in the circuit, the rGO–MMT–PVA ternary bioinspired nano-composites can be used as a conducting wire. A LED red bulb was connected with the power supply, indicating that the rGO–MMT–PVA ternary bioinspired nanocomposites functioned well during the test period. The ternary bioinspired nanocomposites can be tied as a knot but do no harm to it, as shown in Fig. S12,† indicating their great potential application in flexible electronic devices.

2.5. Fire retardant properties

It is known that MMT platelets show good fire retardant properties due to the presence of nitrogen, phosphorus and chlorine.10,11 Thus, the MMT platelets are frequently used for constructing fire retardant nanocomposites. In this work, the rGO-MMT-PVA ternary bioinspired nanocomposites also show good fire retardant properties with only a small amount of MMT present in the resultant nanocomposites. And the thermal stability of the ternary bioinspired nanocomposites is also good, which is confirmed by the thermogravimetric analysis shown in Fig. S5.† Thus, these ternary bioinspired nanocomposites can be used for the protection of flammable biological materials. A silk cocoon placed behind ternary bioinspired nanocomposites did not catch fire even upon prolonged exposure for 5 minutes, and the silk cocoon was burned immediately without the protection of ternary bioinspired nanocomposites, as shown in Fig. 4a and b. When the rGO-MMT-PVA ternary bioinspired nanocomposites were exposed to open flame, the film initially burnt quickly and generated a certain amount of gas due to the presence of PVA and residual oxygen groups of rGO. After that, the ternary bioinspired nanocomposites retain their shape and did not burn any more even when exposed to fire, owing to the formation of an inorganic framework composed of a high content of interlocked MMT nanosheets and rGO sheets.18 SEM images of rGO-MMT-PVA after flame treatment are shown in Fig. 4c and d; the porous structure was formed due to the release of gas from PVA and residual oxygen groups of rGO; meanwhile, a uniform distribution of MMT can also be deduced from the EDS element mapping images.

Conclusion

Inspired by the brick–mortar structure of natural nacre, we fabricated multifunctional ternary bioinspired nanocomposites through synergistic toughening of graphene oxide (GO) and montmorillonite (MMT) nanosheets with poly(vinyl alcohol) (PVA) *via* a vacuum-assisted filtration self-assembly process. The synergistic toughening effect from GO and MMT nanosheets successfully achieved integrated strong and tough ternary bioinspired nanocomposites with a tensile strength of 356.0 MPa, and a toughness of 7.5 MJ m⁻³, which are superior to those of most of the binary GO-based layered materials, respectively. Meanwhile, the bioinspired nanocomposites show high fatigue-resistant, high electrical conductivity and good fire

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retardant properties. This multifunctional ternary bioinspired nanocomposites show great potential applications in the fields of aerospace, flexible electrodes, and flame retardant insulation. And this kind of approach provides a new creative door for constructing multifunctional bioinspired nanocomposites through synergistic toughening in the future.

4. Experimental section

4.1. Materials

Graphene oxide (GO) was prepared by the modified Hummers' method. MMT, which is Na⁺-type montmorillonite purchased from Zhejiang Fenghong Clay Co. Ltd PVA ($M_w = 146\ 000-186\ 000$; hydrolysis = 99 wt%). 57 wt% hydroiodic acid (HI), was purchased from sigma-Aldrich. Concentrated sulfuric acid (98 wt%), hydrochloric acid, sodium nitrate, potassium permanganate, H₂O₂ solution (30 wt%), and ethanol were of reagent grade and purchased from Beijing Chemical Works Co., Ltd. All the reagents were used without further purification.

4.2. Fabrication of ternary bioinspired nanocomposites

3 g MMT was dispersed into 500 ml deionized water and stirred for a week and then centrifuged twice at 3000 rpm for 15 min to obtain a transparent MMT solution. The concentration of the MMT suspension is about 2.8 mg ml⁻¹. PVA powder was dissolved in water at 60 °C under slow stirring for about 1 h and then heated to 92 °C for 10 min to form an aqueous solution (1 mg ml⁻¹). GO was dispersed into deionized water and stirred for 1 h and then subjected to ultrasound for 0.5 h to obtain the GO solution (1 mg ml⁻¹). The obtained MMT solution and PVA solution were successively added to the GO solution at different ratios and then subjected to ultrasound for 1 and 0.5 h to obtain the homogeneous solution, respectively. With vacuum-assisted filtration, the obtained homogeneous solution was self-assembled into the GO-MMT-PVA nanocomposites. After reduction by using HI and then washing with alcohol many times, the rGO-MMT-PVA ternary bioinspired nanocomposites were obtained.

4.3. Characterization

The mechanical properties were tested using a Shimadzu AGS-X at a loading speed of 1 mm min^{-1} with a gauge length of 5 mm. All the samples tested were cut into 20 mm in length and 3 mm in width. Scanning electron microscopy (SEM) images were obtained by using a field-emission scanning electron microscope (JEOL-7500F). Fourier transform infrared (FTIR) spectra were obtained using an iN10MX FTIR instrument. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209F1 Libra under argon with a temperature rising rate of 20 °C min⁻¹. The electrical conductivity was measured by a standard two-probe method using a source meter (Agilent E4980A). X-ray diffraction (XRD) profiles were measured by using an XRD-6000 with Cu K α radiation ($\lambda = 0.154$ nm). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALab220i-XL (Thermo Scientic) with the X-ray source of monochromatic Al Ka. Atomic force microscopy (AFM) images were obtained by

using a Bruker Multimode 8. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G20 instrument at 200 kV. The tensile fatigue tests were performed at a frequency of 1 Hz using the Instron ElectroPulsE1000 test facility; the ratio of the minimum stress to maximum stress was set to 0.1. All the samples tested were cut into 20 mm in length and 5 mm in width.

Acknowledgements

This work was supported by the Excellent Young Scientist Foundation of NSFC (51522301), the National Natural Science Foundation of China (21273017, 51103004), Program for New Century Excellent Talents in University (NCET-12-0034), Beijing Nova Program (Z121103002512020), Fok Ying-Tong Education Foundation (141045), Open Project of Beijing National Laboratory for Molecular Sciences, the 111 Project (B14009), Aeronautical Science Foundation of China (20145251035), State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University (LK1508), and the Fundamental Research Funds for the Central Universities (YWF-15-HHXY-001).

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