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- In situ synthesis of monomer casting nylon-6/reduced graphene oxide
- ² nanocomposites: Intercalation structure and electrically conductive
- ³ properties

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A R T I C L E I N F O

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Keyword: Monomer casting nylon-6(MC nylon-6) Reduced graphene oxide (RGO) Anchoring effect Intercalation structure Electrically conductive network

A B S T R A C T

Based on the industrialized reduced graphene oxide (RGO) product, MC nylon-6/RGO composites were in situ synthesized through anchoring effect of polyetheramine (PEA). Nylon-6 chains were confirmed to intercalate into RGO layers with high grafting ratio by formation of covalent bond and intermolecular hydrogen bond. By presence of PEA, RGO was well exfoliated by the nylon-6 chains and the average layer thickness increased remarkably. Moreover, the stacking of RGO layers was much more weakened and exhibited almost monolayer homogenous dispersion state in the matrix, resulting in the establishment of the electrically conductive network with a low threshold percolation.

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⁶ Introduction

7 Monomer casting (MC) nylon-6, as one of the commercially
8 monoment members of polygmides is synthesized by prioring the 8 prominent members of polyamides, is synthesized by anionic ring-⁹ opening polymerization of caprolactam, using sodium hydroxide
 $\frac{10}{10}$ as catalyst, and diisocyanates as so satalyst. Compared with ¹⁰ as catalyst and diisocyanates as co-catalyst. Compared with $\frac{11}{2}$ ordinary pylon-6 it shows relatively high molecular weight, high ¹¹ ordinary nylon-6, it shows relatively high molecular weight, high $\frac{12}{12}$ crustallinity, resulting in the high mochanical strength excellent ¹² crystallinity, resulting in the high mechanical strength, excellent $\frac{13}{13}$ colf lubricating performance and so on [1] which onables it to be 13 self-lubricating performance and so on $[1]$, which enables it to be $[1]$
14 widely used to replace metallic materials for the production of ¹⁴ widely used to replace metallic materials for the production of $\frac{15}{15}$ are production of $\frac{15}{15}$ ¹⁵ gears, bearings and slide blocks $[2]$. Especially, it is suitable for $\frac{16}{16}$ 16 producing large products that cannot be prepared by injection 17 ¹⁷ molding or compression molding.

¹⁸ Graphene, a single-atom-thick sheet of hexagonally arrayed
 19 and hearded earlier atoms here has under the enatlight symmetry 19 s sp²-bonded carbon atoms, has been under the spotlight owning to ²⁰ its intriguing and unparalleled physical properties $[3]$. Because of
²¹ its nough properties such as overational thermal conductivity high ²¹ its novel properties, such as exceptional thermal conductivity, high $\frac{22}{100}$ Moung's modulus and high electrical conductivity, graphene has 22 Young's modulus and high electrical conductivity, graphene has 23 has bighlighted in fabricating usrious migro-electrical devices 23 been highlighted in fabricating various micro-electrical devices,
24 batteries super capacitors and composites $[4, 5]$ 24 batteries, super-capacitors, and composites $[4,5]$.
25 One of the most fascinating aspects of graphene

²⁵ One of the most fascinating aspects of graphene is the potential $\frac{26}{100}$ for its use in electronic applications due to its very bigh electrical ²⁶ for its use in electronic applications due to its very high electrical
²⁷ conductivity [6] Addition of a small amount of graphene to the conductivity $[6]$. Addition of a small amount of graphene to the insulating nylon matrix can change it into electrical conductor with
a high laugh of electron delectivation quing to the larger surface
 $\frac{29}{2}$ a high level of electron delocalization owing to the larger surface $\frac{29}{30}$
area of the graphene shoots [7]. At a sertain consentration level $\frac{30}{30}$ area of the graphene sheets [7]. At a certain concentration level, 30
lengum as the perselation threshold [9.0], the graphene sheets sap known as the percolation threshold $[8,9]$, the graphene sheets can 31
form a network allowing charge transport and leading to a rapid 32 form a network, allowing charge transport and leading to a rapid $\frac{32}{100}$ rise in the electrical conductivity of the nylon composite $[10]$. 33
Many studies have been reported on the electrical conductivity. 34

Many studies have been reported on the electrical conductivity 34
provement of pylon, composites, with graphene, currently 35 improvement of nylon composites with graphene currently. 35
Boubfid et al. [11] propared BAG/graphene papecheets (CNs) 36 Bouhfid et al. [11] prepared PA6/graphene nanosheets (GNs) 36
nanosomnositos by batch system followed by het compression to 37 nanocomposites by batch system followed by hot compression to 37
ant complex for different to the The electrical maintivity of the 38 get samples for different tests. The electrical resistivity of the 38
composites resolved a highest conductivity value of 2×10^{-7} S/m composites reached a highest conductivity value of 3×10^{-7} S/m 39
and a lowest percelation threshold of 2 wt^{α} graphone content 40 and a lowest percolation threshold of 2 wt% graphene content. $\frac{40}{100}$ Stourer at al. [10] fabricated melt compounding $D6/$ (graphene $\frac{41}{100}$ Steurer et al. [10] fabricated melt compounding PA6/graphene 41
composites based on thermally reduced graphite exide. It was composites based on thermally reduced graphite oxide. It was 42
found that the composites showing a lowest resistivity value of 43 found that the composites showing a lowest resistivity value of 43
14. 10^{4} O cm, and a lowest percelation, threshold of $75w^{10}$ $1.4 \times 10^4 \Omega$ cm and a lowest percolation threshold of 7.5 wt% 44
craphene content. V_{cm} at al. [12] in situ curthosized R 661 45 graphene content. Kim et al. $[12]$ in situ synthesized PA6/ 45
functionalized graphene composites using a thermal reduction. functionalized graphene composites using a thermal reduction 46
of graphite oxide which exhibited a highest conductivity value of 47 % of graphite oxide, which exhibited a highest conductivity value of $\frac{47}{6.84 \times 10^{-4} \text{ S/cm}}$ and a lowest percolation threshold of 0.30 wts 48 6.84×10^{-4} S/cm and a lowest percolation threshold of 0.39 wt% 48
graphene content However the graphene layers with low polarity 49 graphene content. However, the graphene layers with low polarity $\frac{49}{100}$ without modification or functionalization in the above mentioned 50
composites were difficult to be compatible with the bigh polarity 51 composites were difficult to be compatible with the high polarity 51
nylon 6 matrix and were easy to assess in the composites 52 nylon-6 matrix and were easy to aggregate in the composites, 52
resulting in a low electrical conductivity or high percolation 53 resulting in a low electrical conductivity or high percolation ⁵³
threshold Moreover these graphene were small scale propared in 54 threshold. Moreover, these graphene were small-scale prepared in

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⁵⁵ the laboratory, and it is far away from large production and $\frac{56}{2}$ application in industrial scale although it guine perfect π 56 application in industrial scale, although it owns perfect $\pi-\pi$ 57 conjugate structure.

⁵⁸ Reduced graphene oxide (RGO), based on the large production
 $\frac{59}{2}$ in industrial scale is usually reduced by the thermal tratment at ⁵⁹ in industrial scale, is usually reduced by the thermal treatment at $\frac{60}{250}$ temperatures up to $\frac{1050}{25}$ (121). Owner, groups on such PCO 60 temperatures up to 1050 °C [13]. Oxygen groups on such RGO $_{61}^{61}$ surface were difficult to be completely removed during the ⁶¹ surface were difficult to be completely removed during the
⁶² provious reduction of CO to PCO and thus the π g conjugate 62 previous reduction of GO to RGO, and thus the π – π conjugate 63 structure of RCO was inevitably influenced by those oxygen 63 structure of RGO was inevitably influenced by those oxygen
 64 strups However such reactive sites of oxygen groups on its surface 64 groups. However such reactive sites of oxygen groups on its surface
 65 were easy to be designed and controlled to obtain the tailored ⁶⁵ were easy to be designed and controlled to obtain the tailored
 $\frac{66}{100}$ interface by the equal tailores in endea to sufalista BCO and ⁶⁶ interface by the covalent linkage. In order to exfoliate RGO and $\frac{67}{2}$ improve its dispersion in MC pylon 6 matrix, the surface of PCO 67 improve its dispersion in MC nylon-6 matrix, the surface of RGO shorts pools to be proposed to be useful as a polymers before 68 sheets needs to be pre-modified by surfactants or polymers before
 69 the reduction Those surfactants or polymers should be compatible ⁶⁹ the reduction. Those surfactants or polymers should be compatible
⁷⁰ with cantelactam well and inhibit the decrease in toughness of the 70 with caprolactam well and inhibit the decrease in toughness of the 71 polymer composites, resulting from the stress concentration 71 polymer composites resulting from the stress concentration
 72 exuced by the restacling of PCO shorts and most importantly 72 caused by the restacking of RGO sheets, and most importantly,
 73 do not inhibit the anionis ring opening polymorization of MG ⁷³ do not inhibit the anionic ring-opening polymerization of MC
⁷⁴ anion 6. Polyotheramine (PEA) with the molecular woight of ⁷⁴ nylon-6. Polyetheramine (PEA) with the molecular weight of 75 approximately 400, 2000 s/mol is seppresed of floughle obsine of ⁷⁵ approximately 400–3000 g/mol is composed of flexible chains of $\frac{76}{6}$ and $\frac{6}{3}$ contains its problem below with a singular contains or and 76 C-O-C bond in its molecular chain with primary amine as end
 77 example 14.1 which are assigned to an haring offs the farmation $\frac{77}{28}$ group [14], which can easily lead to anchoring effect by formation 78 of covalent bond, intermolecular hydrogen bond or electrostatic 79 ⁷⁹ interactions between the remnant oxygen groups of RGO and PEA 80 molecular chains. As a result, the exfoliation of PCO is improved. $\frac{80}{100}$ molecular chains. As a result, the exfoliation of RGO is improved $\frac{81}{1000}$ and the aggregation of BCO cheets is effectively prevented 81 and the aggregation of RGO sheets is effectively prevented,
 82 reculting in an improvement of electron transfer in the composites ⁸² resulting in an improvement of electron transfer in the composites.
⁸³ Prour provious work, PEA was grafted onto MC pylon. 6 to ophance ⁸³ In our previous work, PEA was grafted onto MC nylon-6 to enhance
 $\frac{84}{100}$ the mechanical tourhases and permanently antistatic property ⁸⁴ the mechanical toughness and permanently antistatic property
⁸⁵ [15] Herein we prepared MC pylon-6/RCO-PEA composites by in 85 [15]. Herein, we prepared MC nylon-6/RGO-PEA composites by in
 86 situ, polymerization. For the effective intercalation of nylon-⁸⁶ situ polymerization. For the effective intercalation of nylon-
 $\frac{87}{2}$ S melasular absins inter the BSO layers. PPA with primary amine as 87 6 molecular chains into the RGO layers, PEA with primary amine as $\frac{88}{2}$ and group is anchored onto PCO surface before the polymerization. ⁸⁸ end group is anchored onto RGO surface before the polymerization
 $\frac{89}{4}$ to strapathen the molecular entangloment with pulse. 6 molecular $\frac{89}{20}$ to strengthen the molecular entanglement with nylon-6 molecular chains $\frac{90}{91}$ chains.

91 In the first step, the graft of RGO by PEA was realized by $\frac{92}{2}$ ultrasonic dispersion of both PCO and PEA in melting caprolac-⁹² ultrasonic dispersion of both RGO and PEA in melting caprolac-
⁹³ tam matrix at 80 °C and a stable colloidal suspension of RGO-93 tam matrix at 80 °C, and a stable colloidal suspension of RGO-
94 **DEA** in cantolactam was obtained. In the second step, the MC 94 PEA in caprolactam was obtained. In the second step, the MC
 95 pylon-6/RCO-PEA composites were in situ synthesized by using 95 nylon-6/RGO-PEA composites were in situ synthesized by using
96 the obtained cannolatam/PCO-PEA mixture without the aid of 96 the obtained caprolactam/RGO-PEA mixture without the aid of 97 columns. The interfecial interaction intercalation structure 97 solvents. The interfacial interaction, intercalation structure 98 and electrically conductive persuadi structure of MC mylen $6/$ 98 and electrically conductive network structure of MC nylon-6/
99 BCO PFA expressive sures investigated. The interaction 99 RGO-PEA composites were investigated. The interaction $\frac{99}{6}$ chains and BCO layers as well as the 100 between nylon-6 chains and RGO layers, as well as the 101 uniform dispersion of BCO and additionally the formation of 101 uniform dispersion of RGO, and additionally the formation of 102 conductive natural are recognished for the improved electrical 102 conductive network are responsible for the improved electrical 103 conductivities conductivities.

¹⁰⁴ Experimental

¹⁰⁵ Materials

¹⁰⁶ The RGO powders were supplied by Sixth Element Materials
¹⁰⁷ Technology Co. Ltd. (Changzhou, China) with an average diameter 107 Technology Co., Ltd. (Changzhou, China) with an average diameter
 $\frac{108}{108}$ of 50 u.m. The CL (caprolactam) monomer was supplied by China ¹⁰⁸ of 50mm. The CL (caprolactam) monomer was supplied by China 109 Petroleum and Chemical Co., Ltd. (Yueyang, China), with a
 110 commercial grade product, NaOH (sodium bydrovide), as the 110 commercial grade product. NaOH (sodium hydroxide), as the 111 catalyst with applytical purity was purchased from Kermel 111 catalyst with analytical purity was purchased from Kermel
 112 Chemical Beagent Co. Itd. (Tianiin China) and TDL (toluene ¹¹² Chemical Reagent Co., Ltd. (Tianjin, China), and TDI (toluene-
¹¹³ 24 diisecunate) as the co-ottalust with analytical purity was 113 2,4-diisocyanate), as the co-catalyst with analytical purity was
 114 purchased from Kelong Chemical Reagent Eactory (Chengdu ¹¹⁴ purchased from Kelong Chemical Reagent Factory (Chengdu, $\frac{115}{115}$ China) PEA with average molecular weight of 2000 s/mal was ¹¹⁵ China). PEA with average molecular weight of 2000 g/mol was
¹¹⁶ purchased from Uunteman Beluurathanes Itd. Cuangribou Branch ¹¹⁶ purchased from Huntsman Polyurethanes Ltd., Guangzhou Branch
¹¹⁷ (Guangzhou China) (Guangzhou, China).

¹¹⁸ In situ synthesis of MC nylon-6/RGO-PEA composites

Firstly, 400 g of CL monomer was put into a three-necked flask 119 and heated to about 80 °C. After completely melting, 8 g of PEA and 120
Ag of PCO powders were added. The mixed melt was stirred for 121 4 g of RGO powders were added. The mixed melt was stirred for 121
20 min, and conjected for 20 min. Then, the melt was refluxed 122 20 min and sonicated for 30 min. Then, the melt was refluxed 122
under vacuum conditions for 20 min to remove water from it 0.6 s 123 under vacuum conditions for 30 min to remove water from it. $0.6 g$ and 123
of NaOH was added under vigorous stirring. The melt was refluxed and 124 of NaOH was added under vigorous stirring. The melt was refluxed 124
under vacuum again and 2.3 g of TDL was added. Finally after 125 under vacuum again and 2.3 g of TDI was added. Finally, after 125
quickly well mixed up the melt was cast into a preheated mould at 126 quickly well mixed up, the melt was cast into a preheated mould at 126
170 °C. The reaction lasted for 60 min and the product of MC pylon- 127 170 °C. The reaction lasted for 60 min and the product of MC nylon-
 C/DC PFA composites were obtained. The resultant MC nylon C_1 = 128 6/RGO-PEA composites were obtained. The resultant MC nylon-6/
RCO-REA composites were designated as MC nylon-6/y RCO-REA 129 RGO-PEA composites were designated as MC nylon-6/x RGO-PEA, 129
where x indicates the weight ratio of RCO in the composite For 130 where x indicates the weight ratio of RGO in the composite. For 130
comparison the part MC pylon 6 and MC pylon 6/PCO samples in 131 comparison, the neat MC nylon-6 and MC nylon-6/RGO samples in 131
absence of PEA were synthesized with the same method. The 132 absence of PEA were synthesized with the same method. The 132
synthesis presence of MC pulse $6/BCO$ PEA sepmesites is depicted 133 synthesis process of MC nylon-6/RGO-PEA composites is depicted 133
in Fig. 1.34 $\frac{134}{2}$

Measurements 135

FT-IR analysis 136
The structures of BCO, π BCO and π BCO BEA samples were 137 The structures of RGO, g-RGO and g-RGO-PEA samples were 137
pluged with a Nicolat EGO Fourier transform infrared enotrom 138 analyzed with a Nicolet-560 Fourier-transform infrared spectrom-
 $\frac{138}{20 \text{ min}^{-1}}$ and the state of the spectrometer (FT-IR) (U.S.A). The scanning rate was 20 min^{-1} , and the 139 differentiate rate was 4 cm^{-1} . 140

Raman analysis 141
The skeletal structures of the PCO α PCO and α PCO PEA and 142 142 The skeletal structures of the RGO, g-RGO and g-RGO-PEA and 142 MC nylon-6 samples were analyzed at room temperature with a 143
RENISIAM lavia Raman misseaseas (UV) suss the sange of 200 RENISHAW Invia Raman microscope (UK) over the range of 300– 144
2000 cm⁻¹ Jacon qualitation acuras at 523 nm uses used 3000 cm^{-1} . Laser excitation source at 532 nm was used. 145

 $X-Ray$ diffraction analysis (XRD) 146
The interlayer spacing of the samples of PCA and $R = \frac{147}{147}$ The interlayer spacing of the samples of RGO, g-RGO and g- 147
O BEA and MC pylon $6/BCO$ BEA composites was measured at 148 RGO-PEA and MC nylon-6/RGO-PEA composites was measured at 148
room temperature over the scanning range approximately of 2×149 room temperature over the scanning range approximately of 2 149
 $A = 3-30^\circ$ with Rigaku D/may III B X-ray diffraction equipment 150 θ = 3–30° with Rigaku D/max III B X-ray diffraction equipment 150
(XRD)(Japan) Conner (Cu) K radiation (λ = 0.154 nm) was used at 151 (XRD) (Japan). Copper (Cu) K_{α} radiation (λ = 0.154 nm) was used at ¹⁵¹
a generator voltage of 40 kV, current of 35 mA, and the scanning ¹⁵² a generator voltage of 40 kV, current of 35 mA, and the scanning 152
speed was $2.4^{\circ}/\text{min}$. The d specing of the PEA CO layers was 153 speed was $2.4^{\circ}/$ min. The *d*-spacing of the PEA-GO layers was 15^3
calculated with the Bragg equation: calculated with the Bragg equation:

$$
2d \sin \theta = n \lambda \tag{1} \tag{1}
$$

where θ is the diffraction angle; *n* is the order of diffraction, and λ 158 is the incident wavelength.

X -ray photoelectron spectroscopy analysis (XPS) 159
The XPS analysis of the PCO α PCO and α PCO PEA Was 160

The XPS analysis of the RGO, g-RGO and g-RGO-PEA was 160
formed with a XSAM 800 spectrometer (KRATOS Co. LIK) using 161 performed with a XSAM 800 spectrometer (KRATOS Co., UK), using 161
AlKa radiation (1486 6 eV) at a pressure of 2.0 \times 10⁻⁷ Pa AlKa radiation (1486.6 eV) at a pressure of 2.0×10^{-7} Pa.

Atomic force microscopy analysis (AFM) 163

164 The sheet dimensions and thickness of RGO, g-RGO and g-RGO-
A were characterized with a Shimadzu SPM9700 atomic force 165 PEA were characterized with a Shimadzu SPM9700 atomic force ¹⁶⁵
misroecome (AFM) (Israel as conded in tegning meda General at 166 microscopy (AFM) (Japan) and recorded in tapping mode. Samples 166
for AFM in take a group are conditionally distributed also halo 167 for AFM imaging were prepared by depositing diluted alcoholic 167
disparation of BCQ and a BCQ BEA (0.1 ma(m)) on frashly 168 dispersion of RGO, g-RGO and g-RGO-PEA (0.1 mg/ml) on freshly 168
closued mics curface 2.2.6 Thermal gravimetric applyeis (TCA) 169 cleaved mica surface.2.3.6 Thermal gravimetric analysis (TGA) 169
The thermal stability and grafting ratio of PCO α PCO and α 170

The thermal stability and grafting ratio of RGO, g-RGO and g- 170
O BEA were moasured with a TA 2050 thermo gravimetric RGO-PEA were measured with a TA 2950 thermo gravimetric 171
analyzer (TCA) (U.S.A.) with the flow rate of 50 ml min⁻¹ under analyzer (TGA) (U.S.A.) with the flow rate of 50 ml min⁻¹ under 172
nitrogen atmosphere. The grapulated samples of about 10 mg were nitrogen atmosphere. The granulated samples of about 10 mg were 173
heated from ambient temperature to approximately 800 °C at a heated from ambient temperature to approximately 800° C at a 174
rate of 10° C min⁻¹ Calibration of the instrument was rate of 10° C min⁻¹. Calibration of the instrument was

ِ متن کامل مقا<mark>ل</mark>ه

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