A study of crystallisation of poly (ethylene oxide) and polypropylene on graphene surface

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ABSTRACT

Crystallisation behaviour of poly (ethylene oxide) (PEO) and isotactic polypropylene (iPP) on graphene surface was investigated by means of polarized microscopy, wide angle X-ray diffraction (WAXD), and Raman techniques. Results indicated that graphene influences the crystallisation and crystal structure of iPP and PEO. WAXD peaks shifting toward lower diffraction angle, i.e. increase in d-spacing, was observed in both PEO and iPP crystallised on the surface of graphene. The change of d-spacing of both PEO and iPP could result from the compressive stress caused by graphene. A shift of 2D band in graphene was observed from Raman spectra. The Raman spectra indicated the big shift in the 2D band is due to the presence of stress induced strain in the polymer attached graphene. The residual stress was generated during crystallization of the polymers on the surface of graphene. Due to the interactions between the graphene and the polymers, the stress was transferred to the graphene which leads to a strain of the graphene. Raman spectra proved the presence of stress generated by the crystallization of the polymers on the surface of graphene.

Introduction

Since the discovery of graphene, it has been received attention as it is a promising materials almost in many areas [1]. Graphene has been applied to polymers as a nano-filler for polymer reinforcement such as for nylon [2], polypyrrole [3], linear low density polyethylene [4], polyurethane [5] polyphenylene [6] etc. Due to its two dimension honey comb single layer crystal lattice structure, graphene has extraordinary properties such as high electron mobility (250,000 cm²/V) [1,7], excellent optical properties [1], high thermal conductivity at room temperature (5000 Wm⁻¹K⁻¹) [8] and excellent mechanical properties [1,9,10]. Compared to other carbon based fillers such as carbon nanotubes, graphene has superior properties and larger surface area which can introduce interactions with the polymer matrix. Therefore, new generation multi-functions polymer nanocomposites could be produced to fit in a wide range of industry applications [11,12].

The incorporation of inorganic fillers can affect the crystallisation behaviour of semi-crystalline polymers such as acting as nucleation agents to accelerate crystallisation [13,14], which will influence the physical properties of the polymer such as optical, mechanical and thermal properties. Crystallisation and the crystal geometry of semi-crystallised polymers play a vital role in the mechanical and thermal properties [12]. The crystallisation behaviour of biodegradable poly (L-lactic acid) (PLLA)/graphene oxide (GO) nanocomposites was studied by Want et al. [15]. GO loading significantly influenced the non-isothermal and isothermal melt crystallisation of PLLA/GO nanocomposites where non-isothermal crystallisation temperature and isothermal melt crystallisation rate first increased and then decreased from 0.5wt% to 2wt% GO showing a peak at 1wt% GO. The isothermal melt crystallisation rate in the nanocomposites was significantly greater than the pure PLLA indicating GO acted as a nucleation agent in PLLA. However, the incorporation of GO did not change the crystallisation mechanism. Xu and his co-workers [16] investigated the effect of incorporating GO nanosheets (GONS) on the isothermal and non-isothermal crystallisation behaviour in isotactic polypropylene (iPP). GONS acted as a nucleation agent in iPP and it significantly increased crystallisation temperature. During isothermal crystallisation process, induction period and half crystallisation time of nanocomposites were significantly reduced. The nucleation density of nanocomposites was much larger than that of the pure iPP and the spherulite growth rate was higher as well. The crystal structure of iPP was not affected by GONS. Solution mixing
method was used to prepare biodegradable poly(ε-caprolactone) (PCL)/thermally reduced graphene (TRG) nanocomposites to in Zheng’s research [17]. TRG introduces heterogeneous nucleation effect in the PCL but did not change the crystallisation mechanism and crystal structure. Significant improvements in storage modulus of the nanocomposites were also reported. A comparative study was conducted by Xu et al. to compare the effects of CNTs and graphene nanosheets (GNSs) on the crystallisation behaviour of PLLA [18]. Their results showed that both CNTs and GNSs could act as nucleation agents to accelerate the crystallisation of PLLA. However, CNTs have stronger effect than GNSs. With increasing the filler loadings from 0.05wt% to 0.1wt%, the induction time of CNTs nanocomposites was shortened but GNSs nanocomposites showed contrary phenomenon.

Although numerous of studies on how the incorporation of graphene affects the crystallisation behaviour of semi-crystallized polymers have been carried out [12,19–22], all the studies only focused on crystallisation behaviour of polymers in composites. The crystallisation behaviour of polymers on the surface of graphene has been rarely discussed. Load transfer efficiency from the polymer matrix to fillers not only depends on the properties of the filler and matrix, but also on the interphase between them [23]. In this paper, an attempt to investigate the crystallisation process of polymers on the surface of graphene was made. A polar polymer, poly (ethylene oxide) (PEO), and a non-polar polymer isotactic polypropylene (iPP) were selected for the study. The aim of the research is to investigate whether graphene can cause the change of crystal structure of PEO and iPP and tension transfer takes place between the polymers and graphene.

2. Experimental

2.1. Materials

Poly(ethylene oxide) (PEO) (average Mn – 100,000) and isotactic polypropylene (iPP) (average Mn – 250,000) were purchased from Sigmas Aldrich (UK). The graphene used was produced by mechanochemical method [24] from expandable graphite in the lab. The expandable graphite was purchased from China Qingdao graphite Company.

2.2. Sample preparation

The preparation of graphene is as follows. Expandable graphite was mixed with powder melamine in volume ratios of 1:1. The mixtures were dispensed into de-ionised water to make solutions with a concentration of 1 g/100 ml. The solutions were then heated up to and kept at 80 °C for 1 h with constant stirring, to allow the melamine to fully penetrate and expand the graphite galleries. After this, the solutions were filtered and dried at 80 °C. The dried mixtures then underwent ball-milling to initially exfoliate the graphite layers, and then dispersed in de-ionised water and underwent further exfoliation with sonication for 1 h (Fisher Scientific Sonic Dismembrator Model 500, 300 W). Hot water was used to repeatedly wash the mixtures to remove the melamine. Fig. 1 shows the transmission electron microscope (TEM) images of the obtained graphene sheets.

Graphene coated glass sheets for optical microscopy characterization were prepared as followed. The graphene was added into 40 ml distilled water in a 100 ml beaker and then the resulted suspension was ultrasonicated for 30 min at room temperature. After ultrasonication, the suspension was subjected to a centrifugation by Thermal Scientific SORVALL BIOFUGE PROMO centrifuge with the speed of 2000 rpm for 20 min. A low concentration suspension was obtained after centrifugation. The suspension was drop casted onto glass sheet, and the coated glass sheet was dried for further use.

2.3. Optical microscopy (OM) characterization

Leico MC170 HD DMLM optical microscopy equipped with a METTLER TOLEDO FP82HT hot stage was used for characterize the crystallisation process of PEO and iPP on the surface of graphene. Crystallisation process at different temperatures was recorded.

2.4. Wide-angle X-ray diffraction(WAXD) characterisation

WAXD was used to study the crystal structure of the PEO and iPP crystallised on the graphene surface. Bruker D2 Phaser WAXD system (Cu – Kα; λ = 1.5418 Å) was used for the study. The diffraction angle 20 was 2°–45° using a 0.02 step size and 0.5 s per step.

2.5. Raman spectroscopy

Raman spectra were recorded using a Renishaw 2000 Raman spectrometer system with a Helium–Neon laser (1.96 eV, 633 nm excitation). The samples prepared as follows. The graphene suspension as described previously was drop casted onto glass sheets and the coated glass sheets were dried in a drying cabinet. iPP and PEO powders were compression moulded into thin films. The as-prepared iPP and PEO films were then melted on the glass slides with and without graphene sheets and crystallised at 124 °C and 49 °C for 20 min in an oven, respectively. Afterwards, the cooled samples were carefully peeled from the glass slides. For the samples with the crystallized polymers, the graphene sheets were transferred to the surface of the polymers after peeling. For comparison,
the glass slides with only graphene casting also underwent the same thermal treatment.

3. Results and discussion

3.1. Optical microscopy analysis of crystallisation

The polarising optical microscopy images of the PEO and iPP crystallised on the graphene and glass surface with crystallisation time are shown in Figs. 2–5. Comparing the polymers crystallised on the graphene and glass surface, it can be seen that the graphene initiates nucleation for both PEO and iPP. Several characteristic types of spherulites can be observed under polarised light. The spherulites can be radial or ringed type depending on the feature of fibrils. The fibrils tend to be straight in radial spherulites whilst twisted around their longitudinal axes in ringed spherulites [25,26]. All the spherulites presented in the polarising optical microscopy images are radial. With the aid of a primary red filter (λ- late) located diagonally between crossed polarizers, the sign of birefringence of the spherulites can be determined [26,27]. When the spherulites are positive, the first and third quarter’s sight are darker and second and fourth quarters of sight are lighter. For

![Polarised optical microscopy images of PEO crystallised at 49 °C on the graphene and glass surface (Left: on glass surface; Right: on graphene surface).](image-url)
negative spherulites, the quarters are arranged in a reversed pattern. It can be observed from the images that the crystals formed on graphene and glass surfaces have different structures. For the PEO, the spherulites formed on glass surface mostly were positive radial spherulites and those formed on graphene were mostly negative radial ones. With increasing crystallisation temperature, the spherulites on glass surface tended to be mixed radial and changed to positive radial ones. In the case of iPP, the spherulites on the glass surface were mixed radial even the crystallisation temperature was changed. The iPP spherulites on the graphene surface were mostly positive radial and the number of fibrils presented in a spherulite increased with increasing crystallisation temperature.

When the crystallisation temperature is high enough, the iPP spherulites on the graphene surface become mixed-radial spherulites.

Plots of average diameters versus time of PEO and iPP at different crystallisation temperatures are shown in Fig. 6. The spherulite growth rate was summarized in Table 1. The results clearly indicate that the graphene has a significant influence on the crystallisation behaviour of the two different polymers. The spherulite growth rate of both PEO and iPP is slower on the graphene surface than on the glass surface which indicates that the graphene could restrain the PEO and iPP molecular mobility. However the influence of graphene on the growth rate is more

Fig. 3. Polarised optical microscopy images of PEO crystallised at 51 °C on graphene and glass surface (Left: on glass surface; Right: on graphene surface).
Plots of nucleus number versus time of PEO and PP at different crystallisation temperatures are shown in Fig. 7. It seems that the presence of graphene induces heterogeneous crystallisation. During crystallization, the number of crystals becomes stable eventually. Before stable period, crystals keep appearing and the number of crystal increases with prolonged crystallisation time. In addition, PEO crystallised on the graphene surface generally entered the stable period faster than that crystallised on the glass surface while iPP crystallised on the graphene surface enter the stable period slower.

3.2. WAXD analysis on the crystal structure of iPP and PEO crystallised on graphene surface

The WAXD spectrums of iPP and PEO crystallised on graphene surface, glass surface and compression mould are shown in Fig. 8. The X-ray peaks of iPP crystallised on graphene surface show much lower intensity which indicated the lower crystallinity of iPP crystallised on the graphene surface. The WAXD results of PEO indicate that the PEO crystallised on the graphene surface has higher crystallinity than on the glass surface while the compression moulded sample has the highest crystallinity. From the iPP X-

![Fig. 4. Polarsed optical microscopy images of iPP crystallised at 124 °C on graphene and glass surface (Left: on glass surface; Right: on graphene surface).](image-url)
Ray pattern, the crystal structure on the graphene and glass surface is regarded as the mixture of α-form and γ-form while that in compression mould is the mixture of α-form and β-form [28] indicating that graphene changed the crystal structure of iPP. The X-ray spectrum of iPP crystallised on the graphene surface exhibits peak shifting toward lower diffraction angle compared to the spectrum crystallised on the glass surface and compression moulded samples. For example, the peak of plane (110) of iPP was shifted from 14.68° to 14.28° when iPP crystallised on the graphene surface. The d-spacing was changed from 6.04 to 6.21 Å and this indicated that the distance between two planes (110) was enlarged when iPP crystallised on the graphene surface. Similarly, the X-ray spectrum of PEO crystallised on the graphene surface also shows peak shifting toward lower diffraction angle. The peak represented plane (120) was shifted from 19.67° to 19.04° and the d-spacing of plane (120) was enlarged from 4.51 Å to 4.66 Å. The shifting of x-ray peak can be caused by strain or stress [29]. The preparation procedure of XRD samples are the same and no

Fig. 5. Polarised optical microscopy images of iPP crystallised at 126 °C on graphene and glass surface (Left: on glass surface; Right: on graphene surface).
chemical reaction was involved. The possible reason for the peak shifting is that the presence of graphene induces the stress that change the d-spacing of iPP and PEO crystals [29]. In addition, enhance surface forces brought by introducing nano-fillers in polymer matrix can change the lattice parameters at nano-scale [30]. The change could be an indicator for the stress transfer between graphene and the polymer chains. In order to confirm this, Raman technique was employed.

### 3.3. Raman spectroscopy

Fig. 9 shows the Raman spectra of the polymers, the graphene, and the graphene with the polymers crystallized on. With crystallization, two obvious changes were observed. Firstly, compared with the pure graphene, the intensities of D band of the graphene with the crystallized polymers attached were significantly increased. Without crystallized polymers, the ratio of intensity of D band to that of G band (I_D/I_G) is as low as 0.107, which proves that the thermal treatment did not affect the graphic structure of graphene and did not induce defects. After the crystallization of polymers on the graphene, I_D/I_G dramatically arose to over 0.55 (list in Table 2). Considering the low I_D/I_G ratio of the G, the rise of D band in G-iPP and G-PEO was not induced by the thermal treatment. Thus, the significant increase of the D band after the polymer crystallized on the graphene surface may be due to the strong resonant Raman coupling and scattering of graphene with the polymers [31–33]. This observation implied strong interaction of the graphene with the polymers. Furthermore, compared with the pure graphene, a shoulder was appeared at the right side of G band for the crystallized polymers attached graphene. The shoulder originates from resonance Raman scattering induced by interaction of the graphene with the polymers [34]. These two observations proved the strong interaction between the graphene and the polymers crystallizing on it. The detailed Raman spectra of graphene and iPP and PEO attached graphene is shown in Fig. 10. Table 2 lists the band positions of all the bands calculated using Lorenz fitting, and ratio of the intensities of the D band to G band. Apart from the changes in D band and G band, the 2D band of the polymer attached graphene became different from the pure one. A stronger shoulder was shown at the left side of the main 2D band for both polymer attached graphene. Furthermore, the main 2D bands shifted to lower position. Double peaks Lorenz fitting

### Table 1

|                | PEO | PP  |
|----------------|-----|-----|
| Crystallisation temperature (°C) | 49  | 124 |
| Surface        | Glass| Glass|
| Spherulite growth rate (μm/s)    | 2.81| 0.71|

### Table 2

|                | PEO 49°C | PEO on graphene surface 49°C | PEO 51°C | PEO on graphene surface 51°C | PEO 53°C | PEO on graphene surface 53°C |
|----------------|----------|-------------------------------|----------|-------------------------------|----------|-------------------------------|
| Crystallisation temperature (°C) | 49       | 51                            | 53       |                               | 53       |                               |
| Surface        | Glass    | Graphene                      | Glass    | Graphene                      | Glass    | Graphene                      |
| Spherulite growth rate (μm/s)    | 2.81     | 2.24                          | 2.61     | 2.23                          | 2.21     | 1.92                          |

Fig. 6. Plots of average diameters versus time obtained from optical microscopy analysis. (a) PEO at 49 °C (b) PEO at 51 °C (c) iPP at 124 °C (d) iPP at 126 °C.
suggests over 3 cm\(^{-1}\) shifting for both the main band and the shoulder band of the both polymer attached graphene. The big shift in the 2D Band is due to the presence of stress induced strain in the polymer attached graphene [35,36]. The residual stress was generated during crystallization of the polymers on the surface of graphene. Due to the interactions between the graphene and the polymers, the stress was transferred to the graphene, which lead to a strain of the graphene. Thus, the Raman spectra prove the presence of stress generated by the crystallization of the polymers on the surface of graphene.

4. Conclusions

Raman, polarized optical microscopy and WAXD were used to investigate the effect of graphene on the crystallisation behaviour of PEO and iPP. The crystallisation behaviour on the graphene surface was highlighted. From polarising microscopy images, the spherulites appeared on the glass and graphene surface were different. The presence of graphene influences the iPP and PEO crystals structure. Graphene can be considered as a nucleating agent to trigger PEO and iPP crystallisation. The spherulite growth rate of both iPP and
PEO decrease on the graphene surface. WAXD spectra reveal the crystal structure of iPP and PEO crystallised on the graphene surface was affected, i.e. the d-spacing is increased. Force transfer from the polymers to graphene surface was involved during crystallisation. Raman spectra indicated the big shift in the 2D band is due to the presence of stress induced strain in the polymer attached graphene. The residual stress was generated during crystallization of the polymers on the surface of graphene. Due to the interactions between the graphene and the polymers, the stress was transferred to the graphene, which lead to a strain of the graphene. Thus, the Raman spectra prove the presence of stress generated by the crystallization of the polymers on the surface of graphene.

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Table 2
Parameters of the graphene bands.

| Sample  | R_G | R_D_all | R_D_main | R_D_shoulder | R_2D_all | R_2D_shoulder | R_2D_main | ID/IG |
|---------|-----|---------|----------|--------------|----------|---------------|----------|-------|
| G       | 1332.1 | 1580.4  | 1580.4   | 2676.0       | 2643.3   | 2685.1        | 0.107    |
| G-PEO   | 1332.1 | 1580.8  | 1579.7   | 1613.7       | 2667.0   | 2640.0        | 2681.6   | 0.593 |
| G-iPP   | 1332.1 | 1580.7  | 1579.5   | 1613.3       | 2669.7   | 2639.9        | 2681.6   | 0.552 |

Fig. 9. Comparative Raman spectra of (a) iso-polypropylene polymer (iPP), graphene (G) and graphene on which the iPP crystallized (G-iPP), and (b) polyethylene oxide polymer (PEO), graphene (G) and graphene on which the PEO crystallized (G-PEO).

Fig. 10. Comparative Raman spectra of (a) graphene (G), graphene on which the PEO crystallized (G-PEO), and graphene on which the iPP crystallized (G-iPP), and (b) detailed spectra of 2D bands.

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