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Expanded graphite nanoplatelets as coupling agents in glass fiber reinforced polypropylene composites



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ABSTRACT

The interfacial adhesion between E-glass fibers and various types of nanomodified polypropylene (PP) matrices have been investigated on single-fiber model composites. In particular, an evaluation of the fiber–matrix interfacial shear strength was performed by the fragmentation tests on model composites prepared by using PP matrices containing various amounts (up to 7 wt%) of expanded graphite nanoplatelets (xGnP).

The presence of xGnP in the polymer matrix resulted in a remarkable increase of the interfacial shear strength values (up to a factor of about 6 for a 7 wt% content of xGnP) if compared to neat PP. Moreover, wettability measurements in various liquids evidenced that the work of adhesion of the polymer matrix with respect to glass fiber, was improved by the presence of xGnP.

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1. Introduction

It has been widely recognized that the fiber/matrix interfacial shear strength is one of the key factors determining the mechanical properties of fiber reinforced composite materials, in particular the fracture resistance parameters [1]. Concurrently, the interphase region often exhibits properties markedly deviating from those of the surrounding bulk matrix [1].

Polypropylene (PP) is one of the most widely used thermoplastic matrices for the production of glass fiber (GF) reinforced composites with excellent performance/cost ratio [2]. Due to the non-polar nature of the matrix, interfacial adhesion is a critical issue for PP/GF composites [3]. In fact, some of the available literature data for uncoupled PP/GF composites, indicate that an interfacial shear strength (ISS) values in the range 1–6 MPa can be considered [4–11]. In a recent study by Yang and Thomason [12], reporting a careful experimental research involving both fiber pull-out and microbond tests, a value in the range 3–4 MPa was provided.

According to the scientific literature, two main strategies have been adopted to improve the fiber/matrix adhesion in PP/glass composites: (i) the development of specific fiber sizings/coatings [4,5,7,8,10,11,13] and/or (ii) the incorporation of coupling agents into the PP matrix [7,8]. Both strategies showed a good capability to improve the fiber/matrix adhesion level.

http://dx.doi.org/10.1016/j.compositesa.2014.06.016 1359-835X/© 2014 Elsevier Ltd. All rights reserved. For example, Thomason and Schoolenberg [10] observed that the use of silane coupling agents have only a slight effect on the improvement of PP/GF interfacial shear strength. Moreover, they experimentally observed that full commercial coating formulation applied to glass fibers is very important for the interface strength: variations of one order of magnitude in PP/GF adhesion were observed depending on the nature of the glass fiber coating. Etcheverry et al. [4,14] evidenced that a chemical anchoring of the PP matrix polymer on glass fibers by direct metallocenic polymerization, may lead to an increase of the ISS with respect to the untreated fibers by a factor of 2.1 [4]. On the other hand, Mäder and Freitag [7] proved that the bond strength in a PP/GF system can be significantly increased by modifications of the PP matrix, such as the addition of polypropylene grafted with acrylic acid or irradiation with electron beams.

Recent investigations demonstrated that nanoparticles homogeneously dispersed in a polymer matrix [15–17] or localized at the interfacial region [18–20] may also promote the fiber/matrix interfacial adhesion in several types of fiber reinforced composites.

In a recent work of our group, it was shown how the addition of both non-functionalized and dimethyldichlorosilane-functionalized silica nanoparticles led to a remarkable (up to a factor of about 5) increase of the interfacial strength in the PP/GF system [21]. The observed effect was explained by considering that the presence of silica nanoparticles cause an increase of the work of adhesion of polypropylene with respect to glass, as proven by wettability tests with various liquids. Concurrently, with the incorporation of nanoparticles an enhancement of the mechanical properties of



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the polymer matrix can be obtained [17] or specific functionalities can be attained [22].

There has been a recent increasing interest in thermoplastic matrices modified with expanded graphite nanoplatelets (xGnP) [23,24]. Most of the research was focused on the preparation method and on the thermo-mechanical characterization, but no investigations can be found regarding the effect of the matrix modification on the interfacial properties in fiber-reinforced structural composites.

Therefore, the aim of this study is to investigate the possibility to improve the adhesion between E-glass fibers and PP by dispersing xGnP in the polymer matrix.

2. Experimental section

2.1. Materials and samples preparation

The PP matrix used in this work was an isotactic homo-polypropylene matrix (code PPH-B-10-FB) produced by Polychim Industrie (Loon-Plage, France) and kindly provided by Lati Industria Termoplastici (Varese, Italy). FUSABOND[®] P M-613-05 maleic anhydride modified polypropylene (PPgMA) was supplied by DuPont[™] de Nemours (Geneva, Switzerland).

Exfoliated graphite nanoplateletes xGnP^{*}-M-5 have been supplied by XG Sciences Inc. (East Lansing, USA). Details on the exfoliation process as well as on the morphology of xGnP can be found elsewhere [25].

E-glass fibers (GFs), designed as RO99 P319, were supplied by Saint-GobainVetrotex (Vado Ligure, Italy) and used as-received. These GFs are indicated as treated with a proprietary silane based coupling agent specifically designed for polypropylene matrices.

Unfilled matrix was denoted as PP, while nanocomposites were designated indicating the matrix, the compatibilizer (if any) with its content, the filler and its amount. For instance, a sample filled with 5 wt% of PPgMA and 5 wt% of xGnP was indicated as PP-PPgMA-5-xGnP-5.

Square sheets (thickness of around 0.7 mm) of PP-xGnP, PP-PPgMA and PP-PPgMA-xGnP were prepared by melt mixing in a Thermo Haake internal mixer (temperature = 190 °C, rotor speed = 50 rpm, time = 10 min) followed by compression moulding in a Carver laboratory press (temperature = 190 °C, pressure e = 0.76 MPa, time = 10 min). Thin (70–80 μ m) matrix films used for the preparation of the microcomposites for the fragmentation test were obtained by a further hot pressing stage (temperature = 200 °C, pressure = 3.4 MPa, time = 10 min).

2.2. Testing methods

2.2.1. Filler characterization

Density measurements were carried out by an helium pycnometer (Micromeritics[®] Accupyc 1330, Norcross USA), at a temperature of 23 °C, using a testing chamber of 3.5 cm³. Surface area and porosity measurements were performed utilizing an ASAP^{*} 2010 Accelerated Surface Area and Porosimetry machine (Norcross, USA) referring to the nitrogen gas physisorption process, setting a saturation pressure of 738.57 mmHg and a bath temperature of 77.35 K.

The morphology of expanded graphite platelets was observed at various magnifications by using a Zeiss Supra 40 (Berlin, Germany) field emission scanning electron microscope (FESEM), at an acceleration voltage of 5 kV.

2.2.2. Single fiber fragmentation tests

Microcomposite samples were prepared by the following procedure. About 10 fibers were aligned between two films of the

selected PP system, sandwiched between two Mylar[®] sheets (thickness of 0.5 mm) and two aluminum plates. The mold was placed in a vacuum oven at a temperature of 165 °C and at a pressure of about 10 kPa for about 20 min and then it was let to cool in air. The specimens were obtained by cutting strips containing one single fiber longitudinally aligned in the centerline. The microcomposites dimensions were roughly 0.18 mm in thickness, 5 mm in width and 25 mm in length. Single fiber fragmentation tests (SFFT) tests were performed at room temperature by using a custommade apparatus represented by a small tensile tester (Minimat, by Polymer Laboratories) placed under a polarized optical stereomicroscope (Wild M3Z by Leica). Tests were performed at a strain rate of 0.05 mm⁻¹. At least five specimens were tested for each sample. All samples were loaded up to a strain of 10% in order to reach the saturation of the fragmentation process. The mean fiber length at saturation, L_s , was measured by means of an image analyzer system ImageJ v.1.46a on optical pictures taken under polarized light. According to Ohsawa et al. [26], the fiber critical length, L_c , was considered equal to 4/3 L_s .

2.2.3. Surfaces energetics and roughness

The wettability of the matrix samples and the glass fiber was measured by contact angle measurements with two different liquids: water as a polar liquid (milli-Q grade, surface tension $\gamma_1 = 72.8 \text{ mN m}^{-1}$, polar component of surface tension $\gamma_1^p = 50.7 \text{ mN m}^{-1}$, dispersive component of surface tension $\gamma_1^d = 22.1 \text{ mN m}^{-1}$, polarity $X_1^p = \gamma_1^p / \gamma_1 = 0.7$), and ethylene glycol as a non-polar liquid (surface tension $\gamma_2 = 48.0 \text{ mN m}^{-1}$, polar component of surface tension $\gamma_2^p = 19.0 \text{ mN m}^{-1}$, dispersive component of surface tension $\gamma_2^d = 29.0 \text{ mN m}^{-1}$, polarity $X_2^p = \gamma_2^p / \gamma_2 = 0.4$) [27].

The total surface tension (γ^{tot}) can be factorized by considering two additive terms: the dispersive surface tension (γ^d) and the polar surface tension (γ^p) :

$$\gamma^{tot} = \gamma^d + \gamma^p \tag{1}$$

The estimation of the surface tension components of matrices with various compositions was done through the geometric mean [27] on the basis of vibration induced equilibrium contact angles (VIECA) [28] measured in both test liquids by a modified Wilhelmy technique. Surface tension components of glass fiber were estimated referring to the advancing contact angles measured by Wilhelmy technique and applying the geometric mean. Knowing the surface tension components of the adherends, the work of adhesion was evaluated using the harmonic mean (W_n^h) equation, applicable to predict interactions between low-energy materials [27]:

$$W_a^h = 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right)$$
(2)

and the geometric mean (W_a^g) equation, more suitable to describe interactions between low-energy and high-energy materials:

$$W_a^g = 2\left(\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p}\right) \tag{3}$$

where the superscripts d and p refer to the dispersive and polar components, respectively, while subscripts 1 and 2 refer to the two solids in contact (polymer and glass fiber), respectively.

The roughness of the samples was determined by a Wave System rugosimeter (Hommelwerke Waveline GmbH, Villingen-Schwenningen, Germany) scanning a 15 mm line at a speed of 0.50 mm min⁻¹. At least three measurements were performed per each sample on the same specimens previously adopted for the estimation of the contact angle. The ANOVA analysis was carried out on the means of R_a and R_{max} at a significance level of 5%.

2.2.4. Composite characterization

Cryogenic fracture surfaces of unfilled PP and PP nanocomposites were observed at various magnifications by using a Zeiss Supra 40 (Berlin, Germany) field emission scanning electron microscope (FESEM), at acceleration voltages between 2.5 and 4 kV.

Transmission electron microscopy (TEM) technique was adopted to analyze cryocut surfaces of PP nanocomposites. A Philips^{*} EM 400 T (Amsterdam, Netherlands) transmission electron microscope, was used at an acceleration voltage of 80 kV. Thin section of PP nanocomposites were ultramicrotomed at a temperature of -100 °C by using a cryo-ultramicrotome.

X-ray diffraction (XRD) analysis was performed by a Rigaku 3D Max X-ray diffractometer operating at the Cu K α wavelength (0.154056 nm), scanning the samples in a 2 θ range between 3° and 67° at a 2 θ step of 0.05°.

Solid-state ¹³C NMR experiments were carried out through a Bruker 300 WB instrument (Bruker Biospin, Italy) operating at a proton frequency of 300.13 MHz. High resolution experiments, characterized by cross polarization with magic angle spinning and variable contact time technique (VCT-MAS), were performed operating at a ¹³C resonance frequency of 75.48 MHz. The spectra were acquired with a 5 s recycle delay, decoupling length $6.2 \,\mu s$ and 200 scans. The samples were packed in 4 mm zirconia rotors, which were spun at 6.5 kHz under air flow. Adamantane was used as external secondary reference. The relaxation times T_{CH} (crosspolarization rate constant) and $T^{H}_{1\rho}$ (¹³C spin–lattice relaxation time) were determined indirectly by the profile decay of all resolved carbon nuclei with the increase of contact-time, which was established in a range varying from 200 to 9000 µs. In particular, intensity signal profiles M(t) were fitted to a one-component equation, assuming that all carbons were in similar motional domains, in according to Eq. (4).

$$M(t) = M_0 \exp\left(-\frac{t}{T_{1\rho}^H}\right) \exp\left(1 - \frac{t}{T_{CH}}\right)$$
(4)

where M_0 is a normalization factor. The two relaxation times obtained from NMR experiments can be directly related to the mobility of the carbons being observed. Low mobility (higher heterogeneity) generally results in shorter T_{CH} and longer $T^{H}_{1\rho}$ values, while a mobility increases (e.g. with increasing amorphous phase or homogeneous character of the material) leads to larger T_{CH} and smaller $T^{H}_{1\rho}$ values. However, since the fitting was not satisfactory in the case of some samples, the decay curve was fitted by a doubleexponential function, in according to Eq. (5).

$$M(t) = M_0 \left[\exp\left(-\frac{t}{T_{1\rho}^H}\right) + \exp\left(-\frac{t}{T_{2\rho}^H}\right) \right] \left[1 - \exp\left(1 - \frac{t}{T_{CH}}\right) \right]$$
(5)

where $T^{H}_{1\rho}$ and $T^{H}_{2\rho}$ represent the long and short spin–lattice relaxation times, respectively [29]. The latter equation is generally used to describe relaxation phenomena in materials showing highly heterogeneous distribution of the filler within the matrix or phase separation.

Differential scanning calorimetry (DSC) tests were carried out by a Mettler DSC30 differential scanning calorimeter under a constant nitrogen flow of 100 ml min⁻¹. The samples were first heated to 200 °C at a rate of 10 °C min⁻¹ and held for 5 min in order to erase any previous thermal history. Crystallization tests with cooling rates of 10 °C min⁻¹ down to 0 °C were carried out. A subsequent heating scan was performed at 10 °C·min⁻¹. The melting enthalpy of 100% crystalline isotactic PP has been considered as $\Delta H^0 = 209 \text{ J g}^{-1}$ [30]. Moreover, the crystallinity χ_c of nanocomposite samples was calculated by taking the weight fraction of PP and PPgMA in the composite into account. The melting temperatures T_{m1} and T_{m2} were recorded during the first and second heating scan, respectively. The crystallization enthalpy ΔH_c was measured by integrating the heat flow curve during cooling scan.

Thermogravimetric analysis (TGA) was carried out through a Q5000 IR thermogravimetric analyzer (TA Instruments-Waters LLC, New Castle, USA) imposing a temperature ramp between 40 and 700 °C at a heating rate of 10 °C min⁻¹ under a constant nitrogen flow of 25 ml min⁻¹. The onset of degradation temperature ($T_{d,onset}$) was determined by the point of intersection of tangents to two branches of the thermogravimetric curve, while the maximum rate of degradation temperature ($T_{d,max}$) was determined from the peak maxima in the first derivative of weight loss curve.

Uniaxial tensile tests were performed with an Instron[®] 4502 (Norwood, USA) tensile machine on samples of at least five ISO 527 type 1BA specimens. The tests were carried out at a crosshead speed of 0.25 mm min⁻¹ up to a maximum axial deformation of 1%. The strain was recorded by using a resistance extensometer Instron[®] model 2620-601 with a gage length of 12.5 mm. The elastic modulus was measured as secant modulus between deformation levels of 0.05% and 0.25% in according to ISO 527 standard. Uniaxial tensile properties, such as stress at yield (σ_y), stress at break (σ_b) and strain at break (ε_b) were determined at an higher crosshead speed (5 mm min⁻¹) without extensometer.

Creep tests were performed utilizing a dynamic mechanical analyzer DMA Q800 (TA Instruments-Waters LLC, New Castle, USA) applying a constant stress (σ_0) of 3 MPa for 3600 s at 30 °C. Rectangular samples 25 mm long, 5 mm wide and 0.20 mm thick were used, adopting a gage length of 11.5 mm. The creep compliance D(t), computed as the ratio between the strain and the creep stress, was plotted against the time for the different samples. Dynamic mechanical analyses (DMA) were carried out at a DMA Q800 testing machine over a temperature range between $-20 \,^{\circ}$ C and 160 °C, imposing a heating rate of 3 °C/min and a frequency of 1 Hz. A preload of 0.2 MPa and a maximum strain of 0.05% was imposed on rectangul samples 25 mm long, 5 mm wide and 0.20 mm thick. The most important viscoelastic functions (*E'*, *E''*, *tan* δ) were recorded at different temperatures.

3. Results and discussion

3.1. Filler characterization

The filler density, obtained through helium pycnometry, resulted to be 1.851 ± 0.018 g cm⁻³. At least 300 measuring cycles were needed in order to reach a constant density value, probably due to packaging and agglomeration of the lamellae which highly hinder the diffusion of helium molecules.

The BET (Brunauer–Emmett–Teller) [31] surface area, calculated from the interpolation of the linear part of the adsorption curve in the plot reporting the adsorbed nitrogen volume versus the relative pressure, corresponded to $32.3 \pm 0.1 \text{ m}^2 \text{ g}^{-1}$. The specific surface area appears quite low when compared to that of other graphite types [32], probably due to the difficult diffusion of nitrogen molecules through graphite packages and agglomerates.

Fig. 1 shows the SEM micrographs of xGnP nanoplatelets, characterized by packages of several sheets with average diameter around 5 μ m. Each package is constituted by layers less than 20 nm thick, with a spacing between layers less than 100 nm.

3.2. Interfacial shear strength evaluation

As reported in a previous work of this group [21], the Weibull strength distribution of the E-glass fibers is characterized by a shape factor m = 5.7 and a scale factor $\sigma_0 = 3609$ MPa (at a



Fig. 1. ESEM images of expanded graphite nanoplatelets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reference length of 15 mm), while the elastic modulus, estimated in accordance with the standard ASTM C 1557-03, is equal to 63 ± 5 GPa.

The average saturation length of the fiber fragments as measured in the single fiber fragmentation tests is reported in Table 1, along with the ISS values estimated according to classical micromechanical models proposed the Kelly–Tyson (ISS_{K-T}) [33] or the Cox (ISS_{COX}) [34] models.

According to the Kelly–Tyson approach the average value of ISS is the result of the static equilibrium between the tensile force acting on a fiber and the shear force transferred through the fiber– matrix interface:

$$ISS = \frac{\sigma_{fb(Lc)}d}{2L_r} \tag{6}$$

where *d* is the fiber diameter and $\sigma_{fb(Lc)}$ is the tensile strength of a fiber at the critical length L_c , which was computed on the basis of the Weibull distribution as:

$$\sigma_{fb(Lc)} = \sigma_0 \left(\frac{L}{L_0}\right)^{-\frac{1}{m}} \Gamma\left(1 + \frac{1}{m}\right) \tag{7}$$

where Γ is the Gamma function, while σ_0 and m are the scale and shape parameters of the Weibull distribution, respectively.

On the other hand, the traditional shear-lag model is developed under the following assumptions: (i) perfectly elastic and isotropic behavior for matrix and fiber, (ii) proportionality between interfacial shear force and the difference between the displacement in the matrix and the displacement that would exist if the fiber were absent, (iii) perfect bonding between matrix and fiber, (iv) same lateral stiffness of fiber and matrix, and (v) no residual stresses. Furthermore, the stress is taken as uniform through a radial section of fiber, and the stress is entirely transferred from matrix to fiber by shear at the interface. The axial stress σ_f in the fiber can thus be written as:

$$\sigma_f = E_f \varepsilon_f \left(1 - \frac{\cosh\left(\beta z\right)}{\cosh\left(\beta t\right)} \right) \tag{8}$$

where ε_f is the far-field applied strain, E_f is the elastic modulus of the fiber, z is the axial coordinate, t is the fiber half-length, while β shear-lag parameter is defined as:

$$\beta = \sqrt{\frac{H}{\pi R_f^2 E_f}} \tag{9}$$

With

$$H = \frac{\pi E_m}{(1 + v_m) \ln\left(\frac{R_m}{R_f}\right)} \tag{10}$$

where E_m and v_m are the matrix elastic modulus and Poisson's ratio, while R_m and R_f are the matrix and fiber radii, respectively. The interfacial shear stress profile $\tau(z)$ can be calculated:

$$\tau(z) = \frac{E_f \varepsilon_f R_f \beta}{2} \left(\frac{\sinh(\beta z)}{\sinh(\beta t)} \right)$$
(11)

It is clear that the addition of PPgMA, xGnP or a combination of both additives produces a sharp decrease of the saturation length and, consequently, an enhancement of the ISS values computed according to both models. Specifically, ISS_{K-T} values obtained by applying the Kelly–Tyson model are plotted in Fig. 2a as a function of the percentage of PPgMA or xGnP for all the investigated samples. As already shown in a previous work of our group, when the PPgMA compatibilizer is added, ISS values considerably increase with respect to the case of neat PP/GF sample [21]. It is interesting to note that comparable improvements can be reached by the addition of graphite nanoplatelets. However, when comparing systems with total weight composition of 10%, the ternary composite PP-PPgMA-5-xGnP-5 exhibits remarkably higher ISS_{K-T} than PP-PPgMA-10, probably thanks to the better filler dispersion and synergistic effect.

The ISS_{COX} values have been also estimated in accordance to Cox model by assuming a concentric cylindrical geometry. The matrix Poisson's ratio, necessary for the implementation of Cox model, was measured on unfilled PP ($v_m = 0.458$) by using two extensometers (axial and transversal) mounted on ISO527 1B specimens

Table 1

ISS values in according to Kelly–Tyson (ISS_{K–T}) and Cox (ISS_{COX}) models and mechanical parameters (E, σ_{br} and ε_{br}) as measured from tensile tests.

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	8	5 5 C C C R=15	(······································		,		
PP4.47 ± 0.312.7 ± 0.23.2 ± 0.61.001546 ± 2435.0 ± 0.116.8 ± 0.3PP-PPgMA-51.20 ± 0.2115.2 ± 2.78.9 ± 1.51.121729 ± 3134.5 ± 0.613.3 ± 0.7PP-PpgMA-100.97 ± 0.3620.2 ± 2.513.9 ± 1.11.071648 ± 1233.6 ± 0.512.1 ± 0.6PP-xGnP-12.24 ± 0.296.7 ± 0.95.7 ± 1.21.151786 ± 3433.3 ± 0.213.5 ± 0.4PP-xGnP-31.46 ± 0.2311.8 ± 1.29.9 ± 1.51.221891 ± 6431.5 ± 0.110.2 ± 0.5PP-xGnP-51.20 ± 0.1115.3 ± 1.312.8 ± 1.71.312020 ± 7731.5 ± 0.49.4 ± 0.3	Sample	L_s (mm)	ISS_{K-T} (MPa)	ISS _{COX} (MPa)	G/G_{PP}	E (MPa)	σ_{br} (MPa)	ε_{br} (%)
PP-PpgMA-51.20 ± 0.2115.2 ± 2.78.9 ± 1.51.121729 ± 3134.5 ± 0.613.3 ± 0.7PP-PpgMA-100.97 ± 0.3620.2 ± 2.513.9 ± 1.11.071648 ± 1233.6 ± 0.512.1 ± 0.6PP-xGnP-12.24 ± 0.296.7 ± 0.95.7 ± 1.21.151786 ± 3433.3 ± 0.213.5 ± 0.4PP-xGnP-31.46 ± 0.2311.8 ± 1.29.9 ± 1.51.221891 ± 6431.5 ± 0.110.2 ± 0.5PP-xGnP-51.20 ± 0.1115.3 ± 1.312.8 ± 1.71.312020 ± 7731.5 ± 0.49.4 ± 0.3	РР	4.47 ± 0.31	2.7 ± 0.2	3.2 ± 0.6	1.00	1546 ± 24	35.0 ± 0.1	16.8 ± 0.3
PP-PpgMA-10 0.97 ± 0.36 20.2 ± 2.5 13.9 ± 1.1 1.07 1648 ± 12 33.6 ± 0.5 12.1 ± 0.6 PP-xGnP-1 2.24 ± 0.29 6.7 ± 0.9 5.7 ± 1.2 1.15 1786 ± 34 33.3 ± 0.2 13.5 ± 0.4 PP-xGnP-3 1.46 ± 0.23 11.8 ± 1.2 9.9 ± 1.5 1.22 1891 ± 64 31.5 ± 0.1 10.2 ± 0.5 PP-xGnP-5 1.20 ± 0.11 15.3 ± 1.3 12.8 ± 1.7 1.31 2020 ± 77 31.5 ± 0.4 9.4 ± 0.3	PP-PPgMA-5	1.20 ± 0.21	15.2 ± 2.7	8.9 ± 1.5	1.12	1729 ± 31	34.5 ± 0.6	13.3 ± 0.7
PP-xGnP-1 2.24 ± 0.29 6.7 ± 0.9 5.7 ± 1.2 1.15 1786 ± 34 33.3 ± 0.2 13.5 ± 0.4 PP-xGnP-3 1.46 ± 0.23 11.8 ± 1.2 9.9 ± 1.5 1.22 1891 ± 64 31.5 ± 0.1 10.2 ± 0.5 PP-xGnP-5 1.20 ± 0.11 15.3 ± 1.3 12.8 ± 1.7 1.31 2020 ± 77 31.5 ± 0.4 9.4 ± 0.3	PP-PPgMA-10	0.97 ± 0.36	20.2 ± 2.5	13.9 ± 1.1	1.07	1648 ± 12	33.6 ± 0.5	12.1 ± 0.6
PP-xGnP-3 1.46±0.23 11.8±1.2 9.9±1.5 1.22 1891±64 31.5±0.1 10.2±0.5 PP-xGnP-5 1.20±0.11 15.3±1.3 12.8±1.7 1.31 2020±77 31.5±0.4 9.4±0.3	PP-xGnP-1	2.24 ± 0.29	6.7 ± 0.9	5.7 ± 1.2	1.15	1786 ± 34	33.3 ± 0.2	13.5 ± 0.4
PP-xGnP-5 1.20±0.11 15.3±1.3 12.8±1.7 1.31 2020±77 31.5±0.4 9.4±0.3	PP-xGnP-3	1.46 ± 0.23	11.8 ± 1.2	9.9 ± 1.5	1.22	1891 ± 64	31.5 ± 0.1	10.2 ± 0.5
	PP-xGnP-5	1.20 ± 0.11	15.3 ± 1.3	12.8 ± 1.7	1.31	2020 ± 77	31.5 ± 0.4	9.4 ± 0.3
PP-xGnP-7 1.14±0.20 16.4±1.8 13.8±2.1 1.44 2222±404 31.3±0.1 8.1±0.3	PP-xGnP-7	1.14 ± 0.20	16.4 ± 1.8	13.8 ± 2.1	1.44	2222 ± 404	31.3 ± 0.1	8.1 ± 0.3
PP-PPgMA-5-xGnP-5 0.59 ± 0.09 39.0 ± 5.7 27.9 ± 2.1 1.98 3058 ± 114 33.5 ± 2.3 7.1 ± 1.0	PP-PPgMA-5-xGnP-5	0.59 ± 0.09	39.0 ± 5.7	27.9 ± 2.1	1.98	3058 ± 114	33.5 ± 2.3	7.1 ± 1.0

L_s: Mean fragment length at saturation.

 $\ensuremath{\mathsf{ISS}_{\mathsf{K}-\mathsf{T}}}\xspace$: $\ensuremath{\mathsf{ISS}}\xspace$ in according to Kelly–Tyson approach.

ISS_{COX}: ISS values in according to Cox model.

 G/G_{PP} : Shear modulus normalized with respect to that of PP.

E: Tensile modulus.

 σ_{br} : Tensile strength at break.

 ε_{br} : Elongation at break.



Fig. 2. ISS values according to (a) Kelly–Tyson and (b) to the Cox's models. (c) ISS for GF/PP matrices in according to Kelly–Tyson model, as function of the thermodynamic work of adhesion W_a calculated using the harmonic (open point) and the geometric (full point) mean equation. (\bigcirc, \spadesuit) PP. (\square, \blacksquare) PP-PPgMA, $(\triangle, \blacktriangle)$ PP-xGnP, $(\diamondsuit, \spadesuit)$ PP-PPgMA-5-xGnP-5. The trend lines describe the linear fitting operated on each group.

produced by injection moulding. Relative ISS_{COX} values, i.e. normalized over the value obtained for neat PP (ISS_{PP-COX}), are plotted in Fig. 2b as a function of the relative shear modulus of the matrix. It is interesting to observe that ISS_{COX} exhibits a significative increase with the matrix stiffness for all samples. Furthermore, PP-xGnP nanocomposites exhibits a slightly higher increase of ISS when compared to PP-PPgMA systems. However, the ternary composite PP-PPgMA-5-xGnP-5 displays relative ISS values remarkably higher than PP-PPgMA-10, probably because of the greater mechanical reinforcement (see Table 1).

Moreover, according to the Cox shear lag model, the observed increase in the stress transfer ability of the interface could be explained on the basis of the matrix stiffening effect caused by the additives (both PPgMA and xGnP). Noteworthy, the samples PP-PPgMA show values of relative ISS progressively increasing with the PPgMA content even though the mechanical reinforcement of the samples with filler content higher than 5 wt% is decreasing.

3.3. Surfaces energetics and roughness

Both the matrix and fiber surface tensions were calculated from measured equilibrium contact angles and from those values the thermodynamical work of adhesion (W_a) was computed and the obtained results are summarized in Table 2. The polar component of the matrix surface tension (γ_p) increased considerably due to the addition of PPgMA, probably due to the emersion of some hydrophilic maleic anhydride groups with high surface energy [35]. PPxGnP systems show a similar increase in γ_p likely because of the surface functionalization of the carbonaceous filler. The dispersive component (γ_d) is slightly higher for all nanocomposites with respect to unfilled PP and increases proportionally to the content of PPgMA or xGnP.

As expected, values of work of adhesion (W_a) calculated using the geometric mean equation are higher then those calculated from the harmonic mean equation [27]. The quantity W_a represents the adhesion energy between solid phases, the higher the work of adhesion, the better the interfacial bonding between fiber and matrix. W_a values of PP-PPgMA blends and PP-xGnP nanocomposites are much greater than that of unfilled PP (Table 2). However, as already stated by Wojuzkij [36] a direct correlation between the work of adhesion and the mechanical adhesion parameters may not apply. In fact, micromechanical tests such as the SFFT are characterized by non-equilibrium phenomena (such as viscoelastic behavior and/or the fracture/yield phenomena of the polymer matrix). Nevertheless, in the present case a very good correlation exists with the experimentally measured ISS_{K-T} values and the work of adhesion (Fig. 2c). Also for ternary composites a further increment in W_a values can be observed which correlates well with the corresponding ISS_{K-T} value.

Moreover, it is important to underline that the contribution of surface roughness to surface properties can be neglected and the differences measured through wettability tests can be mainly attributed to surface chemistry. In fact, the roughness of the matrix films used in this work resulted in the range of $R_a = 0.2 - 0.4 \,\mu\text{m}$ ($R_{max} = 2.5 - 3.6 \,\mu\text{m}$) for all samples. The ANOVA analysis carried out on the mean values of R_a and R_{max} showed no statistically significative differences at a significance level of 5%.

3.4. Spectroscopic analyses

From the SEM micrographs of PP-xGnP-5 sample it can be seen that aggregates of graphite nanopateletes appear quite well distributed within the matrix (Fig. 3a), while most of the graphite packages do not seem to be intercalated (Fig. 3c). The average length (*L*) and thickness (*t*) of aggregates is $9.5 \pm 0.5 \,\mu$ m and $0.5 \pm 0.1 \,\mu$ m, respectively, with a correspondent aspect ratio (*L*/*t*) of 19.0 ± 3.9. The effect of the compatibilizer on the filler dispersion can be noticed in the micrograph of PP-PPgMA-5-xGnP-5

Table 2

Surface	tension	components	botcmitza	from the	mansurad	aquilibrium	contact	angles a	nd thermody	unamic wou	rk of adhesion
Sullace	tension	components	estimateu	mom the	measureu	equilibrium	COIILACL	aligies a	na mermoav	/IIdIIIIC WOI	K OI dullesioli.

Matrix or fiber	$\gamma^p (mN m^1)$	$\gamma^d (\mathrm{mN} \mathrm{m}^{-1})$	$\gamma (mN m^{-1})$	W_a^h (mN m ⁻¹)	$W_a^g (\mathrm{mN} \;\mathrm{m}^{-1})$
PP	$0.1 \pm 0.0 (0.003)$	30.1 ± 0.4	30.2 ± 0.4	53.0	53.9
PP-PPgMA-5	$2.7 \pm 0.2 (0.080)$	31.0 ± 0.5	33.7 ± 0.5	57.8	58.4
PP-PPgMA-10	2.8 ± 0.2 (0.075)	34.6 ± 0.4	37.4 ± 0.4	60.4	61.5
PP-xGnP-1	0.7 ± 0.2 (0.021)	32.4 ± 0.4	33.1 ± 0.4	56.3	57.3
PP-xGnP-3	$1.6 \pm 0.2 (0.043)$	35.7 ± 0.5	37.3 ± 0.5	60.0	61.3
PP-xGnP-5	2.1 ± 0.1 (0.052)	38.3 ± 0.5	40.4 ± 0.5	62.1	63.9
PP-xGnP-7	2.8 ± 0.2 (0.065)	40.3 ± 0.4	43.1 ± 0.4	63.7	66.0
PP-PPgMA-5-xGnP-5	2.2 ± 0.2 (0.052)	39.8 ± 0.5	42.0 ± 0.5	63.9	65.1
GF	$2.0 \pm 0.2 \ (0.079)$	23.3 ± 0.5	25.3 ± 0.5	1	1

 γ^{p} : Polar surface tension component. Values of polarity ($X^{p} = \gamma^{p}/\gamma$) are reported in brackets.

 γ^d : Dispersive surface tension component.

 $\gamma = \gamma^p + \gamma^d$.

 W_a^h : Work of adhesion calculated using the harmonic mean Eq. (2).

 W_a^g : Work of adhesion calculated using the geometric mean Eq. (3).

 ISS_{K-T} : ISS in according to the by Kelly–Tyson approach.



Fig. 3. ESEM image of the fracture surface of (a) PP-xGnP-5 and (b) PP-PPgMA-5-xGnP-5. Higher magnification of graphite packages of (c) PP-xGnP-5 and (d) PP-PPgMA-5-xGnP-5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Fig. 3b) with the intercalation of the matrix within the packages of graphite platelets (Fig. 3d). The graphite nano-layers have been separated to a higher degree with deformed shapes, leading to a significant decrease of the aspect ratio to 6.4 ± 1.7 . This can be attributed to the lower melt viscosity of the compatibilized polymer, resulting in a better inter-diffusivity of the matrix onto the structure of the expanded graphite aggregates which then produces an increase in the melt viscosity and therefore higher shearing of the mixture [37].

TEM images of the sample PP-xGnP-5 and PP-PPgMA-5-xGnP-5 are reported in Fig. 4. Graphite sheets dispersed in the compatibilized matrix (PP-PPgMA-5-xGnP-5) had an average dimension ranging from 100 to 300 nm (Fig. 4b) and appear quite homogeneously dispersed throughout the matrix. On the other hand, it is observed that there are still some graphite sheets existing in micrometer particles in the uncompatibilized matrix (Fig. 4a).

XRD analysis was used to study the crystalline structure of the composites, as shown in Fig. 5a. The diffractogram of xGnP powder presents a strong peak at $2\theta = 26.5^{\circ}$ and a smaller peak at $2\theta = 54.7^{\circ}$, which correspond to the spacing between graphene layers (022) and the (004) crystal orientation, respectively [38]. Furthermore, using Bragg's law and Scherer's equation, the distance between the graphenes that composes the graphite and the size of the crystals formed by them were determined to correspond to 0.334 and 18.91 nm, respectively. In particular, the distance between the graphene sheets is very close to the value reported in the literature (0.335 nm), indicating that the surface treatment did not increase the distance between the graphenes.

Unfilled PP shows the typical peaks reported in the literature at $2\theta = 14.2^{\circ}$, 17.1° , 18.7° and 21.8° , while PP nanocomposites present additional peaks at around $2\theta = 26.5^{\circ}$ and $2\theta = 54.7^{\circ}$ due to the diffraction of the graphene planes. The intensity of the latter peaks is



Fig. 4. TEM images of (a) PP-xGnP-5 and (b) PP-PPgMA-5-xGnP-5 nanocomposites.



Fig. 5. (a) XRD diffractrograms and (b) ¹³C NMR spectrum obtained by CP-MAS-VCT technique for unfilled PP and relative nanocomposites.

Table 3

Results of the CP-MAS-VCT relaxation fit and XRD parameters of unfilled PP and PP nanocomposites.

Sample	$T^{H}_{1\rho}$ (ms) T_{CH} (ms)	<i>d</i> ₀₀₂ (nm)	<i>C</i> (nm)			
	44.2 ppm	26.1 ppm	22.0 ppm			
РР	8.81 ± 0.62 6.08 ± 0.43	9.23 ± 0.63 5.35 ± 0.38	9.37 ± 0.72 5.70 ± 0.42	1	1	
PP-xGnP-1	9.84 ± 0.69 5.81 ± 0.31	10.22 ± 0.96 5.41 ± 0.24	$\begin{array}{c} 10.98 \pm 0.73 \\ 4.85 \pm 0.12 \end{array}$	0.3330	19.62	
PP-xGnP-5	10.96 ± 0.88 3.56 ± 0.18	12.84 ± 0.81 3.15 ± 0.19	13.21 ± 0.74 2.98 ± 0.23	0.3324	34.10	
PP-xGnP-7 ^a	$11.20 \pm 0.52 \\ 0.97 \pm 0.11 \\ 2.10 \pm 0.23$	$14.18 \pm 0.69 \\ 0.80 \pm 0.12 \\ 1.32 \pm 0.21$	$\begin{array}{c} 15.72 \pm 0.62 \\ 0.68 \pm 0.15 \\ 0.94 \pm 0.22 \end{array}$	0.3321	39.72	
PP-PPgMA-5-xGnP-5	10.03 ± 0.69 3.94 ± 0.17	$\begin{array}{c} 11.10 \pm 0.81 \\ 3.80 \pm 0.10 \end{array}$	$\begin{array}{c} 13.20 \pm 0.68 \\ 3.04 \pm 0.17 \end{array}$	0.3323	27.21	

 $T^{H}_{1\rho}$: Spin-lattice long relaxation time. $T^{H}_{2\rho}$: Spin-lattice short relaxation time.

 T_{CH} : Cross-polarization rate constant.

 $d_{002:}$ Spacing between graphene layers.

C: Size of graphite crystals.

^a $T^{H}_{1\rho}$, $T^{H}_{2\rho}$ and T_{CH} are reported successively in column.

proportional to the graphite amount. Moreover, the interplanar distance between graphene layers (d_{002}) and the xGnP crystal size (C)were calculated for PP-xGnP nanocomposites (Table 3). While the interplanar distance does not change significatively in PP nanocomposites, the graphite crystal size increases significatively with the graphite content indicating that some sheets are agglomerating during the compounding of the nanocomposites. On the other hand, the sample PP-PPgMA-5-xGnP-5 shows a smaller crystal size than the sample PP-xGnP-5, indicating that xGnP is better dispersed due to the incorporation of compatibilizer PPgMA, thus corroborating the indications coming from FESEM and TEM observations.

The ¹³C NMR spectrum obtained by VCT-MAS technique is shown in Fig. 5b for unfilled PP and relative composites. Three symmetrical resonance lines, typical of unfilled PP, can be observed with the chemical shifts of 44.2, 26.1 and 22.0 ppm related to CH₂, CH and CH₃ carbons, respectively. Nanocomposite samples show a characteristic broadness of the peaks which increases with the graphite content due to the its high electrical conductivity. On the other hand, no significant change was found in the chemical shifts. Furthermore, the sample PP-PPgMA-5-xGnP-5 produces a spectrum superimposable to that of PP-xGnP-5, probably because the chemical binders related to the maleic anhydride group are lower than the ¹³C NMR sensitivity.

The values of $T^{H}_{1\rho}$ and T_{CH} obtained from the fitting of VCT experimental decay, in according to Eq. (4), are summarized in Table 3 for unfilled PP and its composites. The relaxation values show that the composites have higher molecular rigidity compared to PP. Furthermore, the good fitting quality obtained for composites containing 1 and 5 wt% graphite indicates that the graphite is quite homogeneously dispersed within the matrix. Moreover, the values observed for the sample PP-PPgMA-5-xGnP-5 show higher homogeneity and consequent higher nanofiller dispersion when compared to the sample PP-xGnP-5. In particular, a greater degree of exfoliation can be hypotisized, supporting the results obtained by XRD analyses and electron microscopy observations.

On the other hand, since the fitting using Eq. (4) was not satisfactory in the case of the sample PP-xGnP-7, two spin–lattice relaxation times $(T^{H}_{1\rho} \text{ and } T^{H}_{2\rho})$ and the cross-polarization rate constant (T_{CH}) were obtained by applying Eq. (5) reaching a better fitting accuracy. The results of the fitting obtained for the latter sample indicate highly heterogeneous distribution of graphite within the matrix with diffuse segregation phenomena (high density of aggregates and agglomerates).

3.5. Thermal analyses

In binary PP nanocomposites the addition of xGnP produces a significative increases of the crystallization temperature,

Table 4

DSC and TGA parameters on unfilled PP and xGnP nanocomposi	ites
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approaching a plateau for xGnP content as high as 5 wt% (Table 4). As already shown in similar works regarding compatibilized PP nanocomposites [37,39], when the compatibilizer is added the crystallization temperature tends to increase and the increment is greater for higher PPgMA contents. Furthermore, a slight decrease is shown in PP-PPgMA-5-xGnP-5 samples, probably due to the increased interaction between the compatibilized PP and the nanofiller which may retard the migration of the PP chains onto the growing crystal nucleus. Concurrently, the melting temperature recorded during the second scan (T_{m2}) is slightly higher for PP nanocomposites, while the crystallinity (χ_c) does not seem to depend on the nanofiller addition.

The thermal resistance parameters detected in TGA measurements on PP-xGnP nanocomposites showed that both $T_{d,onset}$ and $T_{d,max}$ markedly increase with the filler content (Table 4). Moreover, the addition of PPgMA further increases the degradation temperatures of PP, probably due to a better dispersion and exfoliation of the graphite nanolayers which produces a greater thermal shielding of the matrix [37].

3.6. Mechanical tests

As reported in Table 1, the addition of graphite nanoplatelets induces a significant increase of the elastic modulus of the PP matrix, which is further incremented by the incorporation of PPgMA, reaching an overall improvement of 98% for the ternary system, compared to unfilled PP. In general, the stress at break decreases with the addition of xGnP, probably because of the filler aggregation and the stronger interaction [40]. For the same reason the elongation at break exhibited by nanocomposites is lower than that of unfilled PP.

Quite surprisingly, only few papers on the creep behavior of polymer composites containing xGnP can be found in the open scientific literature [41–44], but none of them refer to thermoplastic matrices such as PP. In Fig. 6 the isothermal creep compliance of unfilled PP and PP nanocomposites, under a constant load of 3 MPa and at 30 °C, is reported. The introduction of graphite nanoplatelets leads to a remarkable improvement of the creep stability of the material, further enhanced by the incorporation of PPgMA (see Table 5). As often reported in the scientific litera-

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Sample	T_{m2} (°C)	ΔH_{c} (J/g) (χ_{c} (%))	Cryst. Peak T (°C)	$T_{d,onset}$ (°C)	$T_{d,max}$ (°C)	Char (%)
РР	165.1	102.0 (48.8)	115.6	392.9	438.4	0.1
PP-PPgMA-5	163.08	100.7 (48.2)	117.0	406.9	446.2	0.1
PP-PPgMA-10	162.84	100.3 (48.0)	117.9	407.3	446.6	0.1
PP-xGnP-1	165.2	102.2 (49.4)	120.1	424.8	544.6	0.7
PP-xGnP-3	165.3	102.1 (50.4)	123.2	426.0	456.7	2.6
PP-xGnP-5	165.9	100.4 (50.6)	124.0	427.3	458.0	4.6
PP-xGnP-7	166.0	97.8 (50.3)	124.2	430.1	461.4	6.2
PP-PPgMA-5-xGnP-5	166.0	100.1 (50.4)	122.3	444.3	467.2	4.3

 T_{m2} : Melting temperature recorded during the second scan.

 ΔH_c (χ_c): Crystallization enthalpy and normalized crystallinity.

Cryst. Peak T: Crystallization peak temperature.

 $T_{d,onset}$: Onset degradation temperature.

 $T_{d,max}$: Max degradation rate temperature.

Char (%): Residual weight percentage.

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reep compliance data and dynamic mechanical properties of PP and xGnP nanocomposites (f = 1 Hz).	
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Sample	D_e (GPa ⁻¹)	$D_{ve,2000s} ({ m GPa}^{-1})$	$D_{tot,2000s} (\text{GPa}^{-1})$	<i>E</i> ′ (-20 °C) (MPa)	<i>E</i> ′ (23 °C) (MPa)	<i>E</i> " (23 °C) (MPa)	$T_{\beta_{peak}}$ (°C)
PP	0.85	1.24	2.09	3674.4	2063.1	90.3	9.9
PP-PPgMA-5	0.82	1.22	2.04	4155.1	2340.0	115.3	9.1
PP-PPgMA-10	0.85	1.25	2.10	3925.2	2268.3	108.7	9.1
PP-xGnP-5	0.63	0.70	1.33	4148.7	2341.4	106.3	8.9
PP-PPgMA-5-xGnP-5	0.58	0.36	0.94	5350.2	3056.5	143.9	9.1

D_e: Elastic creep compliance.

D_{ve,2000s}: Viscoelastic creep compliance at 2000 s.

Dtot.2000s: Total creep compliance at 2000 s.

E' (-20 °C): Storage modulus at -20 °C.

E' (23 °C): Storage modulus at + 23 °C.

E" (23 °C): Loss modulus at + 23 °C.

 $T_{\beta_{ment}}$: Temperature of β peak recorded in *tan* δ plot.



Fig. 6. Creep compliance (D(t)) of unfiller PP and PP nanocomposites $(T = 30 \circ C, T)$ σ_0 = 3 MPa).

ture, we may assume that nanoparticles effectively restrict the motion of polymer chains, influencing the stress transfer at a nanoscale, with positive effects on the creep stability of the material [45]. The introduction of the nanofiller produces an enhancement of E' both in the glassy and in the rubbery regions, while the glass transition temperature of PP nanocomposites ($T_{\beta_{max}}$), usually referred to the β relaxation, is slightly lower than that of unfilled PP due to the presence of the nanofiller.

4. Conclusion

Interfacial shear strength was investigated by means of the single fiber fragmentation test on various PP/GF microcomposites containing expanded graphite nanoplatelets. Experimental results show that the strength at the interface can be remarkably increased by the addition of xGnP, and that the improvement is further enhanced when the nanoplatelets are used in combination with PPgMA in ternary composites. The work of adhesion computed between fiber and matrix showed a good correlation with the ISS values. In addition, graphite nanoplatelets promoted a remarkable enhancement of both elastic modulus and creep stability of the selected polypropylene matrix. The polymer morphology, investigated through FESEM, XRD and NMR techniques, indicated better homogeneity and interaction in composites added with PPgMA.

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