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Improvement of viscoelastic, elastic and plastic properties of Poly(L-lactide)/Graphene Oxide-Graft-Poly(L-lactide) nanocomposites by modulation of grafted chain length

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Abstract

The full potential of poly(L-lactide) (PLLA) reinforced with graphene oxide, GO, nanocomposites tends to be hindered by aggregation of the nanofillers. In order to promote a good dispersion of GO in the PLLA matrix, polymer grafting techniques have been explored to anchor PLLA onto functionalized GO surface to produce GO-PLLA hybrids. For this purpose, PLLA with a terminal triple bond was synthesized by ring-opening polymerization. By controlling the concentration of monomer to initiator, PLLA samples with three different chain lengths have been prepared and later coupled to azide-functionalized GO using click chemistry. These hybrids were then mixed with commercial PLLA and cast films have been prepared. The ensuing nanocomposite films were studied using Depth Sensing Indentation and the results have shown that PLLA matrix-filler interaction can be modulated by controlling the chain length of PLLA graft. This is a critical point

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because the enhancement of these interactions provides a stronger matrix-filler interphase which improves the stress transfer between both phases and increases the contribution of the interphase to the stiffening of the nanocomposites. Therefore, it has been proven that judicious functionalization of GO is an effective procedure for improving the strength, the stiffness and the creep resistance of the PLLA composites.

Keywords

Polymer-matrix composites (PMCs), Mechanical properties, Hardness testing

1 Introduction

Poly(lactic acid) or poly(L-lactide) (PLLA) is an environmentally friendly aliphatic polyester which is commercially available and has been used for many years in the textile and packaging industry [1]. However, neat PLLA cannot be directly used in some demanding applications because of some limitations such as brittleness, low rate of crystallization, low thermal resistance and permeability to gas [2, 3, 4]. To overcome such limitations nanoparticles have been widely added to the polymer matrix to improve the properties [5]. Different types of nanofillers have been used with PLLA such as layered double hydroxides, layered silicate clays[6], carbon nanotubes [7], as well as other forms of carbon based materials including graphene and graphene oxide. Gonçalves et al have reviewed the production methods and effects of loading on the properties of PLLA/carbon based nanomaterials and outlined the need for a better understanding of the role of nanofillers physico-chemical properties and alignment on the nanocomposites performance, as well as the relevance of synthetic strategies involving the polymerization in the presence of carbon based nanofillers in order to enhance dispersion and increase the level of interactions with the polymeric matrix [8].

As regards the particular case of graphene oxide, both "grafting from" and "grafting to" methods have been used to prepare covalent graphene-polymer conjugates. Xiong et al have reported the functionalization of GO with low molar mass PLLA via the grafting-from approach which lead to improved dispersibility of the nanofillers in PLLA and enhancement of the mechanical properties of the resulting nanocomposites [9]. This enhancement was attributed to mechanical interlocking of the grafted chains and those of the PLA matrix and is in line with the results reported by Baimark

and Srissuwan [10]. In turn, the "grafting-to" approach combined with click chemistry in the functionalization of GO allows better control over polymer chain length as well as the possibility of using pre-formed copolymers to prepare hybrids [11]. In our previous work [12], following a similar synthetic strategy to that of [11], we have concluded that short chain length and immobilization of the polymers were the main reasons for the limited crystallization. Consequently, in the present study, hybrids with different chain lengths and nanocomposites with two levels of loadings have been prepared and the ensuing nanocomposites characterized.

Mechanical characterization of polymeric based systems can be achieved by means of Depth Sensing Indentation (DSI) methods [13, 14, 15]. Particularly, it has been proven that DSI techniques allow getting simultaneously information about different aspects of the elastic, plastic and viscoelastic behavior of both PLLA matrix nanocomposites [16, 17] and polymeric matrix nanocomposites reinforced with carbon fillers [18, 19, 20, 21]. As the depth of the indentations ranges from some tens of nm to some μm, DSI has been used to characterize samples of small dimensions like coatings, thin films [14] or even monolayer graphene [22]. Hence, DSI has been the selected experimental technique to show some results about the influence of functionalization of GO nanoplatelets on the reinforcement of films of PLLA matrix nanocomposites. The aim of this paper is to gain a deeper understanding of the effect of the enhanced interaction polymer matrix-nanofiller resulting from the functionalization of GO on the mechanical properties of the films as determined by means of DSI methods. Particularly, the influence of the length of PLLA chains grafted to GO based fillers on some of the elastic, plastic and viscoelastic properties of the PLLA matrix nanocomposites has been analyzed.

2 Experimental

2.1 Materials

Injection molding grade PLLA, used as polymeric matrix, was kindly supplied by Corbion Purac. This PLLA presented Mn~100 kDa (as determined by SEC against PS standards) and dispersity of 1.3. Commercial GO suspension in water (4.0 g/L) was purchased from Graphenea (Spain). This suspension was frozen inside PP tubes and lyophilized for 48 h to obtain dry GO flakes. Sodium azide NaN$_3$, (Aldrich) and CuSO$_4$·5H$_2$O (JMGS) were used as received. Sodium ascorbate was obtained by neutralization of ascorbic acid. All solvents used were of analytical grade. DMF was dried over

activated molecular sieves 3A, for 24 h, before using.

2.2   Preparation of alkynyl-PLLA

Poly(*L*-lactide) with a terminal triple bond, alkynyl-PLLA (aPLLA) samples with three different molar masses were prepared by ring-opening polymerization using 4-butyn-1-ol as initiator. A bifunctional system comprising N,N-Dimethylaminopyridine and its adduct with trifluoromethanesulfonic acid (DMAP/DMAP.TfOH) was selected as catalyst to obtain the shorter-chain aPLLA sample (PLLA5.5K) while 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was used for the other two longer-chain samples (PLLA15K and PLLA22K). The procedures were already described in previous papers [11, 12].

2.3   Graphene oxide azidation

Dry GO flakes (500 mg) were dispersed in dry DMF (125 ml) in a round-bottom flask. NaN_3 (500 mg) was then added and the suspension was left stirring for 48 h at 40 °C.

   The solid material was then centrifuged at 15000 rpm and washed through redispersion/centrifugation cycles using fresh DMF, then water, acetone and finally CH_2Cl_2. The azidated GO ($GO-N_3$) was obtained after drying overnight at room temperature.

2.4   Preparation of GO-g-PLLA hybrids

The generic procedure for the tethering of aPLLA (5.5K, 15K or 22K samples) to $GO-N_3$ was performed as follows. In a round-bottom flask, $GO-N_3$ (400 mg) was dispersed in dry DMF (40 ml) with aid of sonication. The mixture was bubbled with dry N_2 for 30 minutes. Next, aPLLA (800 mg), $CuSO_4 \cdot 5H_2O$ (200 mg) and sodium ascorbate (430 mg) were added to the flask, which was stirred for 6 h at room temperature. The solid GO-g-PLLA material was recovered by centrifugation at 15000 rpm and washed as described above.

2.5   Preparation of reinforced PLLA films

For each of the GO-g-PLLA samples with different chain length, thick films of reinforced PLLA were prepared with several loads of hybrid material, ranging from 0 to 1% (base: graphene oxide fraction). For this purpose, PLLA and the adequate amount of each GO-g-PLLA were weighed in a vial to a total weight of 400 mg, and 8 ml of dry chloroform were added. The mixture was

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stirred until complete dissolution of the polymer and sonicated for 30 minutes using an ultrasound probe set to a 25 W power output. The homogenized mixture was poured into a flat, levelled PTFE square mold (65 mm × 65 mm) and the solvent was left to evaporate overnight inside the fume hood. The film was detached from the mold and assembled between the plates of a large Petri dish (to keep it flat) and was finally placed inside an oven at 105 °C for 6 hours, in order to remove the solvent completely. The thicknesses of the films were determined according to ISO 2178 using a coating thickness gauge CM-8820 and ranged from 70 to 80 μm with an uncertainty of ± 2 μm.

The reinforced films are named according to Table1.

2.6   DSC measurements

The thermal properties of the materials prepared (in film form) were carried out on a modulated differential scanning calorimeter, TA Instruments MTDSC2920, connected to a liquid nitrogen cooling system and calibrated with different standards. Runs were performed at standard mode. The sample weights were around 6-8 mg for all the specimens. A temperature range from 0 to 220 °C has been studied and the used heating rate was 20 °C/min. The melting temperatures and glass transition temperatures were determined from the first heating cycle. For crystallinity determinations, a value of 93.6 J/g has been taken as the enthalpy of fusion of a perfectly crystalline material [23]. The relative error in the determination of the degree of crystallinity is ±5%.

2.7   Depth Sensing Indentation, DSI, measurements

DSI measurements were carried out by means of a Shimadzu DUH211S hardness tester equipped with a diamond Berkovich indenter at room temperature (23 ± 1 °C). The measurements were performed with the application of a maximum preset load of 10 mN at a loading rate of 1.46 mN/s, after reaching the maximum load, it was maintained for 5 s, then, the load was released with an unloading speed of -1.46 mN/s and, finally, a 0.02 mN load was hold for 5 s. The load-penetration curves were analysed using the Oliver-Pharr method [24] and assuming that the Poisson ratio, ν, of PLLA equals 0.4. This assumption is based on the fact that, according to the literature, ν of PLLA range from 0.35 to 0.45 [16, 25, 26] and on the fact that the error in the DSI mechanical properties arising from uncertainties of the ν values of the indented materials is relatively small [27]. The results of these calculations were corrected taking into consideration the viscoelastic nature of the

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mechanical response of polymers following the procedure suggested by Feng and Ngan [28]. In order to apply this correction, the creep rate at the end of holding of the maximum load was determined using the KWW relaxation function [29] as suggested in [17]. The previously described experimental conditions were selected in order to minimize the creep factor that should be applied for correcting the results [25]. Each measurement was replicated six times at least and the reported properties are the average values.

3   Results and discussion

Firstly, some considerations about the relationships between the size of the indentations and the scales of heterogeneity of the distribution of the nanofillers should be presented. Figure 1 shows a micrograph of 22K05 sample that is similar to those that can be obtained from the other samples. These photographs illustrate the presence of remnant micrometric agglomerates of either GO or modified GO-g-PLLA, a fact that confirms the previous observation about the partial dispersion of these GO based fillers in PLLA matrices [12]. The examination of the photographs seems to indicate that these agglomerates appear to be homogeneously distributed. Taking into account that, under our experimental conditions, the lengths of the diagonals of the DSI indentations are close to ten μm, the characteristic scale of the distribution of these agglomerates must be determined for assuring the representativity of the indentation measurements.

According to the results of the image analysis, the mean diameter of the GO agglomerates that can be appreciated by means of optical microscopy techniques ranges from 5 to 10 μm and the mean distance between two neighbour remnant micrometric GO particles is of the order of a few tens of μm. Two conclusions can be derived from these characteristic distances of the distribution of the filler agglomerates. The first one is that the DSI measurements lead to an average of the properties of matrix and fillers because the size of the agglomerates and the distances between them are not much greater than the diagonal of the indentations [19]. The latter one is indentations should be spaced some hundreds of micrometers apart in order to obtain representative results of the bulk mechanical properties of the nanocomposites. Hence, the DSI measurements were replicated by displacing the indenter along a random walk with X and Y movements that were normally distributed between 100 μm and 1 mm.

Figure 2 shows the load-depth curves that were obtained after indenting the neat polymeric matrix and the GO10 and 22K10 PLLA based nanocomposites. It can be seen that the maximum depth of these indentations ranges

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from 1.2 to 1.6 μm. As the ratio of the thicknesses of the films to these depths is greater than 40, it can be concluded that neither the hardness [30] nor the indentation modulus [31] were affected by the substrate. Figure 2 also indicates that the polymeric matrix is more easily indented than the nanocomposites, a fact that illustrates the reinforcing effect of the nanofillers. Moreover, it also suggests that the functionalized GO-g-PLLA hybrid increases the resistance to indentation more efficiently than GO nanofiller does. In order to discuss quantitatively these effects, the results of the DSI measurements have been collected in Table 2. These values are the averages of six measurements and the uncertainty has been determined as the confidence interval for these mean values (95% confidence level). As could be expected, the uncertainties in the determination of the mechanical parameters of nanocomposites are significantly greater than those of the neat PLLA film used as reference which reflects the fact that the reinforced samples are heterogeneous at the scale of tens of micrometer.

Before analysing the results in Table 2, it is important to remark that nanofiller content is not the only structural parameter that controls the mechanical behavior of PLLA based nanocomposites as it has been reported that the mechanical properties of the PLLA matrices and, particularly, the indentation hardness and modulus of PLLA depend on the crystalline structure of PLLA, on the degree of crystallinity [25] and on the physical ageing of the amorphous phase [32]. Taking into account that, according to XRD results [12], the crystal structure of PLLA is α-form for all the studied films, the PLLA polimorphism influence on the mechanical properties of these films has not been considered. The levels of crystallinity of the samples as determined by means of DSC measurements were collected in Table 3 that shows that the differences on the crystallinity level of the nanocomposites is in the order of few percents, a behaviour that is analogous to that reported in [9]. According to the literature data, the variations of Hit and Eit of PLLA due to an 1% increment of crystallinity (for crystallinity degrees ranging from 30 to 60%) are close to 1 MPa and 0.01 GPa, respectively [25] and, therefore, the expected effects of the crystallinity differences among the studied samples (see Table 3) are significantly smaller than the observed reinforcement effects of the GO based filler (see Table 2). Hence, the influence of the crystallinity on the mechanical properties of the nanocomposites will be disregarded in the following discussion. As the samples were stored at room temperature for more than a year before being DSI tested, all the studied specimens should be completely relaxed (the order of magnitude of the relaxation time for the physical ageing of semicrystalline PLLA is a few days [32]). Consequently, the effect of physical ageing on the mechanical properties of the samples will not be considered for explaining the results of the DSI experiments that have

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been collected in Table 2.

The data in Table 2 show that the rigidity of the nanocomposites as measured by the indentation modulus, Eit, increases as the GO based filler content rises, a behaviour that is analogous to that reported for polymeric matrix nanocomposites reinforced with carbon based fillers, nanoclays, layered silicates or other inorganic nanofillers (see Tables 1 to 6 in [20]). In order to evaluate the reinforcing effect of the GO based fillers, it is interesting to consider the ratios of the properties of the nanocomposites (propc) to those of the neat PLLA matrix (propm). According to Figure 3, the ratios Eitc/Eitm range from 1.4 to 1.7 for the samples reinforced with 1% w/w of GO and GO-g-PLLA hybrids. These ratios are close to those reported by Young et al [33] for the increment of the elastic moduli of rigid polymers reinforced with 0.5% v/v graphene based fillers and to those reported by Díez-Pascual et al [20] for the increment of Eit of different polymer nanocomposites reinforced with 1% w/w of functionalized GO. If one considers that the density of graphene and graphene oxide doubles approximately that of polymeric matrices, fillers contents in 0.5% v/v and 1% w/w can be properly compared and the similarities of the results mentioned above prove that, although GO based nanofillers are not completely dispersed in the PLLA matrix, the enhanced interaction between the GO-g-PLLA and PLLA matrix can promote a noticeable improvement of the elastic properties of the studied nanocomposites. In order to explain these remarkable increments of rigidity is important to take into account that it has been proven by means of nanomechanical analysis that monolayer graphene based fillers do not necessarily give the best reinforcement effect [33].

The relative increment of rigidity due to each different filler can be defined by $\Delta E_r = (Eitc/Eitm - 1)/filler\ content$. The examination of the data in Table 2, seems to indicate that ΔE_r values tend to diminish as the GO based phase percent increases. Similar saturation behaviors have been reported for other nanocomposites systems reinforced with either carbon based or inorganic fillers [33, 34]. These results are in line with those reported by Quiles-Díaz et al who have found that the curve that shows the dependence of the Eit of graphene reinforced polypropylene nanocomposites on nanofiller percent displayed a maximum for 2% v/v of functionalized graphene [21].

As can be appreciated from Figure 3, the relative increment of the indentation moduli of these nanocomposites not only depends on the GO content but also depends on the nature of the nanofillers. The results seem to indicate that the stiffening effect due to the dispersion of the filler rises if the molar mass (Mw) of the grafted PLLA chains, Mw-gPLA, grows. Consequently, all the discussed results about the modulus of these nanocomposites suggest that the PLLA matrix-filler interaction can be modulated by control-

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ling the grafting process. This is a critical fact because the enhancement of these interactions provides a stronger matrix-filler interphase and improves the stress transfer between both phases. The improvement of the matrix-filler interactions due to the functionalization raises the contribution of the interphase to the stiffening of the nanocomposite, an effect that, according to micromechanical description of Wan et al. [26], can be modeled by an increased effective volume fraction of the GO based nanofiller.

In addition to changes in Eit, Table 2 seems to indicate as well that both Martens, HMs, and indentation, Hit, hardnesses rise if the GO-based nanofiller content increases. Furthermore, according to Figure 4, the ratios of Hit of nanocomposites with 1%GO to Hit of neat matrix yield values that vary within 1.5 and 2, which are similar to those reported for different graphene reinforced polymer nanocomposites by Díez-Pascual [20]. Provided that the hardness Hit is related to strength, the increments of the Hitc/Hitm ratio can be also compared to the ratio of the ultimate tensile strengths of PLLA-GO nanocomposites to that of the polymeric matrix, that has been reported to be approximately 1.5 [26]. The closeness of the reinforcement ratios of these nanocomposites and those that have been published previously, points to the fact that, despite the presence of remnant aggregates of GO based fillers, grafting PLLA to the GO hybrids is an adequate strategy for increasing the resistance to permanent deformation of the PLLA matrix.

Figure 4 suggests that the hardening effect due to the solution-casting dispersed GO-g-PLLA hybrids increases with increasing length of the PLLA chain that have been grafted to the GO platelets. These results seem to indicate that the strengthening effect of the GO-based nanofillers diminishes as their content increases. It is interesting to remark that these comments about the strengthening effect of the GO-g-PLLA hybrids parallel the previous ones about the stiffening effect of these nanofillers and, hence, they appear to support the previous statements regarding the enhancement of the interactions matrix-filler due to the grafting of PLLA chains to the GO nanoplatelets.

DSI tests not only provide information about the elastic and plastic properties of the studied nanocomposites but also contitutes an adequate experimental technique for studying other aspects of their mechanical behaviour such as creep. During the holding period of the maximum load of the indentation experiments on polymeric materials, the indentation depth increases because of the viscoelastic nature of these materials. These indentation creep (cit), can be measured as the percentage of change of the indentation depth [14]. The effect of the dilution in PLLA of GO based nanofillers on cit for the studied specimens can be described by considering the values that have been collected in Table 2. These results seem to suggest that the creep resistance of

the nanocomposites is clearly larger than that of the neat PLLA matrix but, apparently, there are no significant differences among the various nanocomposites that have been studied. In order to gain a deeper understanding about the creep during the maximum load maintenance period of DSI experiments, it is important to keep in mind that, although the maximum load is the same in all the experiments, the mean contact pressure of the indenter as measured by the Martens hardness, HMs, is different. To introduce the effect of the contact pressure, a kind of indentation pseudo-compliance, J*it, should be considered by dividing the creep deformation by HMs. This definition of J*it parallels that of compliance, J, as determined by means of creep experiments [35] that equals the quotient of the creep deformation and the stress. Figure 5, that illustrates the dependence of J*it on creep time for three of the studied specimens, seems to indicate that indentation creep of these nanocomposites can be described successfully by means of the KWW relaxation function [29] and suggests that the modification of the GO can increase the resistance to creep of the nanocomposites. This trend seems to be confirmed by Figure 6 that shows the variation of the ratio of the J*it of nanocomposites to that of the matrix after 5 s of maintenance of the maximum load as a function of Mw-gPLA.

Figure 6 shows trends that are similar to those previously discussed for the variation of the indentation modulus and hardness: J*it decreases with increasing length of PLLA chains grafted to the GO platelets and the decrement is more important for the samples with 0.5% w/w content of GO base nanofiller than for those with 1%. Hence, these results point to the fact that the enhancement of the matrix-filler interaction by means of the control of the molar mass of the grafted PLLA chains not only is an adequate method for modulating stiffness and strength of the nanocomposites but also allows to control their resistance to creep.

4   Conclusions

GO-PLLA hybrids were successfully prepared by anchoring alkynyl-PLLA with different chain lengths onto azide-functionalized GO surface by click chemistry. These hybrids were used to prepare nanocomposite cast films of GO-PLLA in commercial PLLA. DSI tests were performed to provide information about the elastic, plastic and viscoelastic properties of these films. It has been shown that the stiffness, the strength and the creep resistance of the nanocomposites increase as the weight percent of the GO based filler rises and that the relative enhancement of the mechanical properties diminishes for the higher GO percent. Even more, it has been observed an increment

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of the mechanical properties of nanocomposites if the molar mass of the grafted PLLA chains grows for a fixed filler content. This observation seems to indicate that the PLLA matrix-filler interaction can be modulated by controlling the chain length of the grafted PLLA chains and suggests that the funcionalization provides a stronger matrix-filler interphase, improves the stress transfer between both phases and raises the contribution of the interphase to the stiffening of the nanocomposites. Hence, the results evidence that functionalization of GO and the control of the molar mass of the grafted PLLA chains is an effective method for enhancing the matrix-filler interactions and modulating the stiffness, the strength and the creep resistance of the PLLA matrix.

Acknowledgements

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Tables:

Table 1: Designation of the reinforced samples (Mw-gPLLA reads for the molar mass of the grafted PLLA chains)

Sample	GO05	GO10	05K05	05K10	15K05	15K10	22K05	22K10
GO content (% w/w)	0.5	1	0.5	1	0.5	1	0.5	1
Mw-gPLLA (kDa)	0	0	5.5	5.5	15	15	22	22

Table 2: Martens (HMs), and indentation (Hit) hardnesses, indentation modulus (Eit), and indentation creep (cit) of the neat PLLA and GO and GO-g-PLLA reinforced nanocomposites.

Sample	HMs (MPa)	Hit (MPa)	Eit (GPa)	cit(%)
PLLA	122±5	203±7	2.9±0.1	8.7±0.2
GO05	170±50	240±70	3.7±0.4	6.5±0.9
GO10	180±10	330±30	4.2±0.3	5.5±0.6
05K05	180±10	350±30	3.8±0.1	5.8±0.8
05K10	200±20	370±30	4.2±0.3	5±1
15K05	200±10	370±10	4.4±0.1	5.3±0.3
15K10	230±70	400±100	4.5±1.5	5±2
22K05	200±50	400±60	4.6±0.4	5.5±0.7
22K10	240±20	440±50	4.8±0.1	5.1±0.4

Table 3: DSC results obtained for the various composite films (Tg and Tm read for the glass transition and melting temperatures, respectively, ΔHm, for the melting enthalpy and Xcm, for the crystalline fraction of the films)

Sample	Tg (°C)	Tm (°C)	ΔHm (J/g)	Xcm(%)
PLLA	70	175	45.8	49
GO05	67	176	47.3	51
GO10	68	175	52.7	57
05K05	69	175	46.9	50
05K10	70	175	43.9	47
15K05	68	175	47.5	51
15K10	69	175	43.5	47
22K05	69	175	40.6	44
22K10	70	175	43.3	47

Captions to Figures:

Figure 1: Micrograph illustrating GO-g-PLLA hybrids dispersion in sample 22K05 sample (original image was processed and binarized using ImageJ software [36])

Figure 2: DSI load-indentation curves for the neat PLLA matrix, GO10 and 22K10 nanocomposites.

Figure 3: Stiffening, Eitc/Eitm, effect of the GO (Mw-gPLLA = 0) and GO-g-PLLA hybrid nanofillers as a function of Mw of the grafted PLLA chains (the dashed lines are just guides for the eye).

Figure 4: Hardening, Hitc/Hitm, effect of the GO (Mw-gPLLA = 0) and GO-g-PLLA hybrid nanofillers as a function of Mw of the grafted PLLA chains (the dashed lines are just guides for the eye).

Figure 5: Indentation compliance, J*it, of neat PLLA and GO10 and 22K10 nanocomposites as a function of the creep time, t_{creep} (lines that represent the best fits of the data to the KWW function have been drawn)

Figure 6: Relative decrease of the compliance of the nanocomposites, Jit*c/Jit*m, due to the GO (Mw-gPLLA = 0) and GO-g-PLLA hybrid nanofillers as a function of Mw of the grafted PLLA chains (the dashed lines are just guides for the eye).
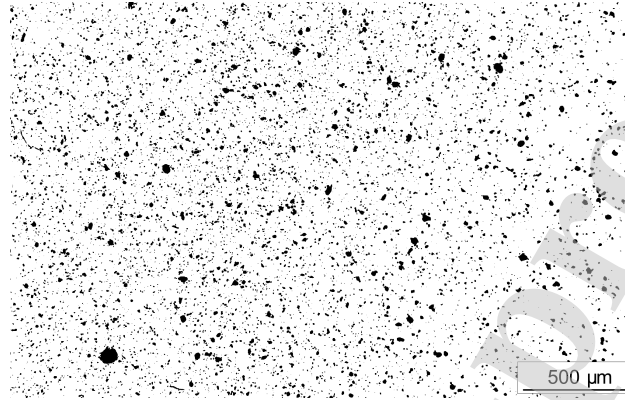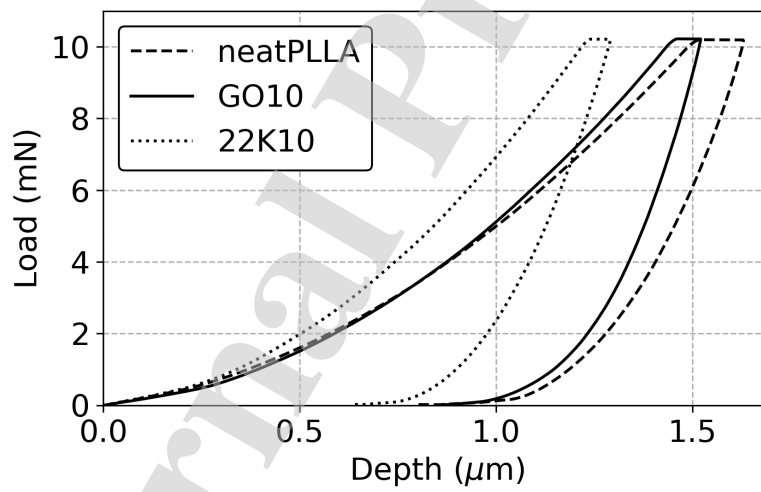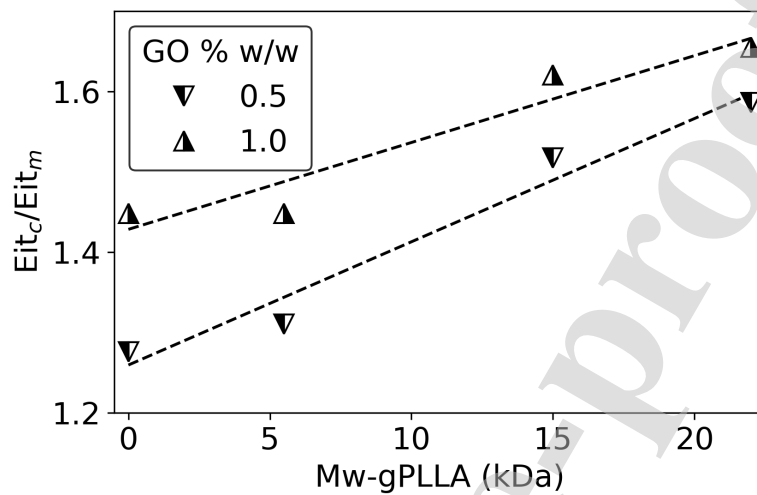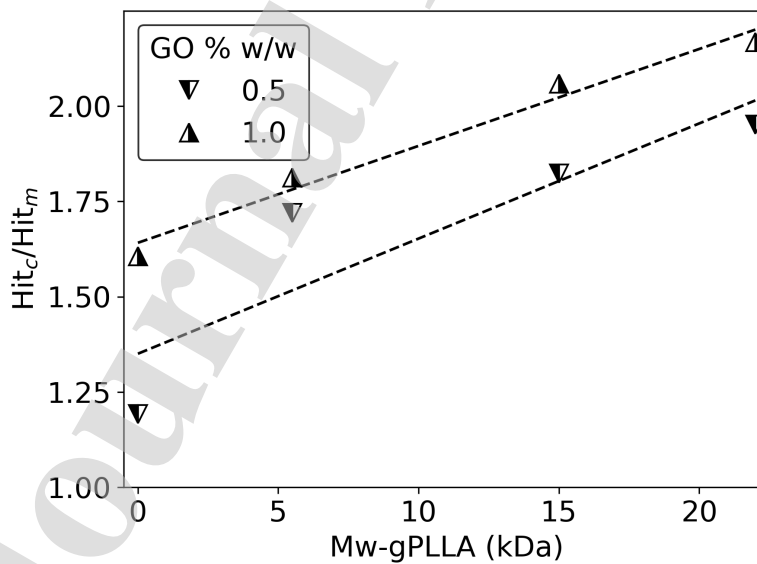
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Figures:

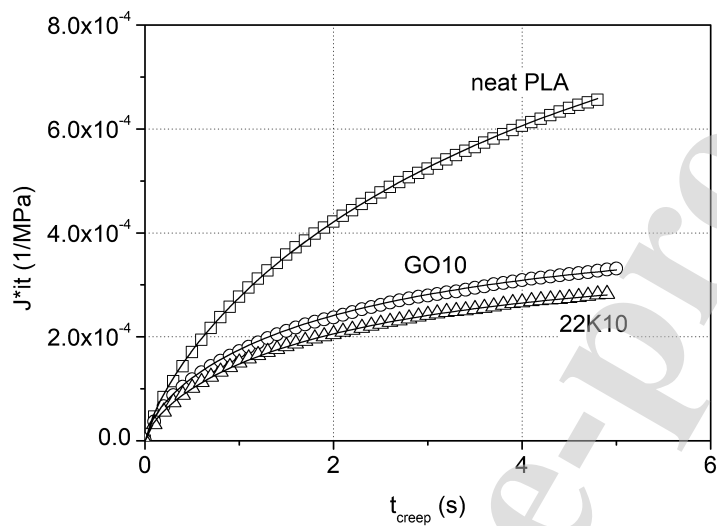Figure 1:

Figure 2:

Figure 3:
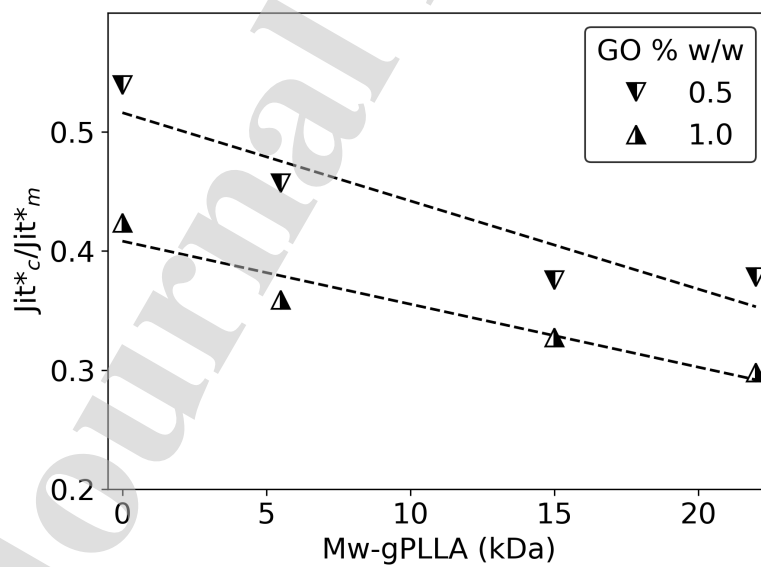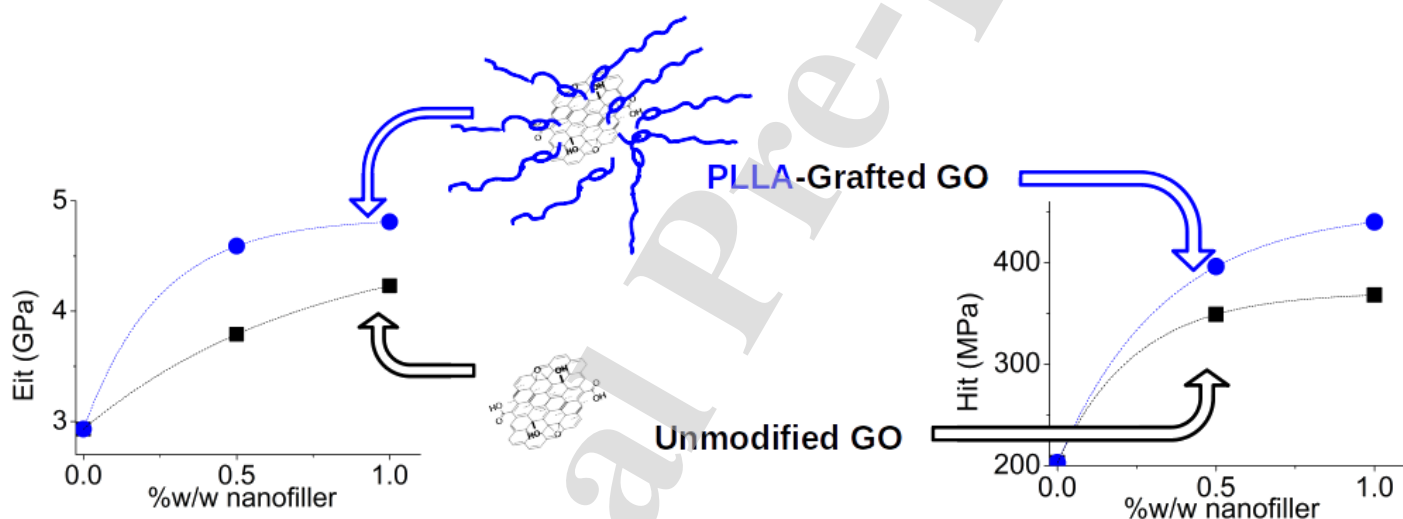

Figure 4:

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Figure 5:

Figure 6:

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.