PRESSIN-AND-FOLDING FOR THE PREPARATION OF EFFICIENT AND HIGHLY LOADED 2D MATERIALS-BASED POLYMER NANOCOMPOSITES

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Abstract

The exploitation of the mechanical potential of 2D materials in nanocomposites is still highly challenging, especially for filler loadings higher than 0.1 vol.%, mainly because of filler dispersion issues. Our work aimed at developing a new technique able to prepare 2D materials-based polymer nanocomposites with high filler dispersion and orientation in order to achieve the expected mechanical properties theoretically predicted at different filler loadings. The technique consists in folding and pressing a sample for a desired number of cycles using a hot-press at a temperature slightly above the melting point of the polymer matrix, hence the name “pressing and folding” (P&F). Compared with melt blending techniques combined with static mixers for the preparation of multi-layers nanocomposites, the P&F technique allows the blending of materials with very different flow behaviours, thus enabling the preparation of layered nanocomposites starting directly from pure polymers and 2D nanofillers in a powder state.

1. Introduction

2D material-based polymer nanocomposites are polymers containing fillers with dimensions below 100 nm and a single-layer of atoms (such as graphene). Despite the significant amount of research in 2D nanofillers since the introduction of polymer-clay nanocomposites two decades ago, it has proven to be difficult to exploit the potential properties of these fillers in nanocomposites [1,2]. This has been particularly an issue for filler loadings higher than a few percent [3,4], mainly because of poor dispersion and agglomeration [1,3–7].

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The concept of the Baker's transformation has been employed in many industrial approaches by means of particular static mixers to efficiently mix together substances otherwise immiscible or hardly mixable [8,9]. This approach has also been used for the preparation of layered nanocomposites containing aligned graphite nanoparticles (GNP) or graphene in melt-blending techniques using multilayer coextrusion [10–12]. However, the nanofiller needs to be already dispersed inside the polymer in a masterbatch, because these techniques do not allow an efficient mixing of materials with different flow behaviour.

Our work aims to develop a new technique able to prepare 2D nanofiller-based polymer composites with good filler dispersion and orientation in order to achieve optimal mechanical properties at both low and high filler loadings. The technique based on the Baker's transformation consists of repeatedly folding and pressing a sample for a number of cycles in a hot-press at a temperature slightly above the melting point of the polymer matrix, hence the name "pressing and folding" (P&F).

Here we show how the P&F technique progressively improved the dispersion and distribution of a 2D filler material (graphite nanoplatelets, GNP) in a planar orientation throughout the volume of a thermoplastic polymer matrix (linear low-density polyethylene, LLDPE). The increase in filler dispersion with P&F cycles was reflected in the electrical and mechanical properties of the nanocomposites. Nanocomposites prepared with the P&F technique showed similar reinforcing efficiencies for low as well as high filler loadings, demonstrating the potential of the Baker's transformation technique in creating well dispersed and aligned nanocomposites for a wide range of filler concentrations without the use of compatibilizers.

2. Materials and methods

Linear low-density polyethylene Flexirene® MS20A (LLDPE) and expanded graphite Timrex® C-THERM™ 002 (EG) were used as polymer matrix and nanofiller for P&F samples, respectively.

The pressing-and-folding technique used for the preparation of P&F nanocomposites consisted in gradually mixing LLDPE and GNP by repeating several times the cycle of folding and pressing each sample at 40 bar for 30 seconds inside a hot-press (Collin P 300 E) at 120°C (melting point of LLDPE = 115°C).

In order to study the properties of a nanocomposite as a function of the P&F cycles – corresponding to GNP dispersion and distribution throughout the matrix volume – a series of LLDPE samples containing a fixed loading of GNP was prepared at 10, 20, 30, 40, 50, 100, 150, 200, and 500 P&F cycles. At last, a series of LLDPE samples containing different amount of GNP was prepared at 200 P&F cycles to validate the effectiveness of this technique.

The microstructures of the nanocomposites were studied analysing the cross-sections of cryogenically broken samples by a scanning electron microscopy (SEM, FEI Inspect-F). The specimens were previously gold-sputtered to cover them with a conductive film 6-8 nm thick.

Electrical conductivity measurements were performed in-plane and out-of-plane of the samples by a 2-points-probe connected to a DC system power supply (Agilent 6614c 0-100V/0-0.5A), and a picoammeter (Keithely 6485). Five specimens per sample were tested both for in-plane and out-of-plane measurements. Length, width, and thickness of each specimen were measured and recorded before testing.

Tensile tests were executed following the ASTM D 638-02a standard method with specimen type V, performing five specimens per sample in a universal testing machine (Instron 5566). The elastic modulus of each specimen was determined by the slope of a linear fit of the stress-strain curve executed over a strain range of 0.25% after the Toe's region. The yield point was considered as the first zero-slope point on the stress-strain curve.

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3. Results

In order to investigate any effect of the P&F technique on the properties of the polymer matrix, a series of pure LLDPE samples was prepared at different P&F cycles. Tensile tests revealed that the properties of pure LLDPE (Young's modulus, yield point, and break point) were unaffected by P&F cycles. Therefore, the sample prepared at one P&F cycle was taken as reference for comparison with nanocomposites' properties (see **Table 1**).

Table 1. Reference mechanical properties of pure LLDPE.

	Young's Modulus (MPa)	Stress at yield (MPa)	Strain at yield (%)	Stress at break (MPa)	Strain at break (%)
LLDPE	140 ± 5	7.85 ± 0.27	22.5 ± 1.0	9.5 ± 0.7	890 ±140

The microstructures of the nanocomposites clearly shew that GNP were being distributed throughout the matrix volume with the number of P&F cycles (see Figure 1). At low number of P&F cycles, samples were characterised by the presence of large and isolated GNP agglomerates, which decreased in thickness and width as the P&F cycles were increased, and the GNP particles contained inside these agglomerates appeared to be oriented mainly parallel to plane of the samples. Finally, samples prepared above 200 P&F cycles presented homogeneous distribution of well-dispersed GNP oriented parallel to the plane of the samples.

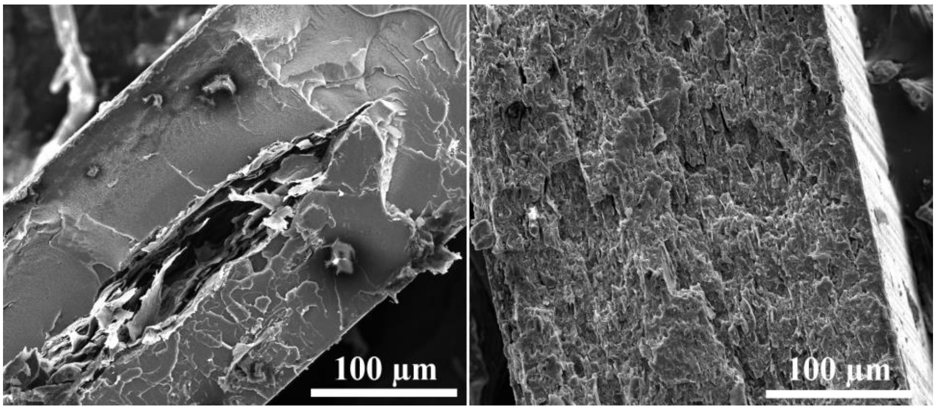

Figure 1. Cross-sections of LLDPE + 0.21 vol.% GNP nanocomposites after 10 and 500 P&F cycles.

The increase in filler dispersion with P&F cycles was reflected in the electrical and mechanical properties of the nanocomposites. For example, the in-plane electrical conductivity of a series of LLDPE + 4.8 vol.% GNP nanocomposites was reduced from $3\cdot10^{-3}$ S/cm to $2\cdot10^{-9}$ S/cm after 500 P&F cycles, while the mechanical reinforcement (i.e. the ratio between the Young's moduli of the nanocomposite and the neat matrix) increased from 1 to 2.3 after 500 P&F cycles. A similar increase with P&F cycles was found also for the yield stress and stress at break. Moreover, the out-of-plane conductivity was always 3-4 orders of magnitude lower than the one in-plane because of the anisotropic microstructure of the nanocomposites.

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The P&F technique was further validated for a series of LLDPE samples containing different loadings of GNP prepared at a fixed number of P&F cycles (200). These nanocomposites showed similar reinforcing efficiencies (i.e. the ratio between an experimental mechanical reinforcement and a theoretical reinforcement that can be predicted by composite models, such as Halpin-Tsai [13], at a particular filler loading) for low as well as high filler loadings, demonstrating the potential of the P&F technique in creating well dispersed and aligned nanocomposites for a wide range of filler concentrations without the use of compatibilizers.

5. Conclusions

The pressing-and-folding technique is a valuable technique for the production of 2D materials-based nanocomposites. We showed how the P&F technique gradually mixed two materials with different flow behaviours, such as a LLDPE polymer and a powder of GNP, overcoming the issue of static mixers used in coextruders for the preparation of layered nanocomposites.

The microstructures of the P&F nanocomposites observed by SEM revealed that the GNP were increasingly distributed and dispersed throughout the polymeric matrix with the number of P&F cycles, and mainly orientated on the plane of the samples. This finding was confirmed by electrical conductivity measurements: although LLDPE is a good insulator, a high in-plane conductivity was found for samples prepared at low P&F cycles. For each sample, the out-of-plane resistivity was 3-4 order of magnitude higher than the one in-plane. As the GNP dispersion and distribution were further increased by the P&F cycles, the electrical conductivity decreased. The effect of GNP dispersion reflected also on the mechanical properties of the nanocomposites: the mechanical reinforcement, yield stress, and stress at break increased with the number of P&F cycles.

Finally, it was shown that nanocomposites could be prepared with a high nanofiller concentration, and still they could show a mechanical reinforcement even without a coupling agent between filler and matrix.

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