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STRETCHING THE ENDURANCE BOUNDARY OF COMPOSITE MATERIALS: PUSHING THE PERFORMANCE LIMIT OF COMPOSITE STRUCTURES

Fibrillar polymer–polymer composites: morphology, properties and applications

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Abstract Micro- or nano-fibrillar composites (MFCs or NFCs) are created by blending two homopolymers (virgin or recycled) with different melting temperatures such as polyethylene (PE) and poly(ethylene terephthalate) (PET), and processing the blend under certain thermo-mechanical conditions to create in situ fibrils of the polymer that has the higher-melting temperature. These resulting fibrillar composites have been reported to possess excellent mechanical properties and can have wide ranging applications with suitable processing under controlled conditions. However, the properties and applications very much depend on the morphology of created polymer fibrils and their thermal stability. The present paper develops an understanding of the mechanism of micro-/nano-fibril formation in PE/PET and polypropylene (PP)/PET blends by studying their morphology at various stages of extrusion and drawing. It is revealed that this subsequent mechanical processing stretches the polymer chains and creates fibrils of very high aspect ratios, thus resulting in superior mechanical performance of the composites compared to the raw blends. The study also identifies the primary mechanical properties of the main types of MFCs, as well as quantifying their enhanced resistance to oxygen permeability. Furthermore, the failure phenomena of these composites are studied via application of the modified Tsai–Hill criterion. In addition to their usage as input materials in different manufacturing processes, possible applications of these fibrillar composites in two different areas are also discussed, namely food packaging with controlled oxygen barrier properties and biomedical tissue scaffolding. Results indicate a significant scope for using these materials in both areas.

Introduction

Reinforced polymer composites are used in a wide variety of applications as they can demonstrate the ability to meet a vast range of (often complex) performance demands. The significant majority of these materials are reinforced with some type of glass or carbon fibre, as this has traditionally provided the composite with the greatest improvements in mechanical properties. Nonetheless, it is well known that there are several drawbacks to the use of these inorganic reinforcing structures, including complex production techniques, high materials and labour costs and environmental impact. This paper reviews the progress of a new type of fibril reinforced polymer composite, derived from immiscible polymer blend pairings that because of their poor mechanical properties are traditionally regarded as worthless.

A number of detailed and comprehensive reviews of polymer blending have been undertaken over the past decades [1–10] and on the whole it is a widely studied and relatively well understood topic that is of interest to many sectors of industry [11]. These reviews establish several important issues that one needs to be aware of when blending polymers, not the least of which is the strong relationship between the morphological structure of a blend and its mechanical and physical properties [5]. It is widely known that the blending of multiple polymers can have the advantage of both improving and tailoring specific material and functional properties [12, 13] but that this occurs

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predominantly in miscible blend pairings, which are less common because the vast majority of polymer blends are thermodynamically immiscible and create weakened multiphase systems.

Immiscible blends have been considered undesirable for much of their history on account of these weak inter-phase boundaries producing poor mechanical properties. One method of overcoming the problem of immiscibility is to produce a tailored blend morphology able to negate its effects [12, 13]. When two immiscible polymers are blended, they often create a partnership whereby the majority constituent (*the matrix*) forms a homogeneous body in which the minority constituent (*the reinforcement*) is dispersed. Just as in an ordinary composite, the quality of this dispersion as well as the strength of the matrix–reinforcement interface are the determining factors for the mechanical properties of the final material. The size and morphology of the suspended polymer phase are crucial to the final physical properties of the blend and can vary tremendously depending on the choice of polymers and the dispersion method employed. For example, the creation of a blend containing well-dispersed spheres can increase the impact resistance of the matrix material, whereas sheet-like inclusions have the ability to greatly enhance the barrier properties of a film and fibres can provide significant increases to unidirectional strength [14]. Furthermore, by using the correct combination of manufacturing and post-processing conditions it is possible to generate all of these reinforcement morphologies from a single immiscible blend pairing.

While this lack of chemical interaction between the blend constituents is generally considered a disadvantage for traditional polymer blending, it is a critical element in the successful creation of a new type of fibrillar polymer–polymer composite from immiscible blends. Microfibrillar reinforced composites (MFCs) are comprised of an isotropic polymer matrix reinforced with an even dispersion of high aspect ratio micro or nanofibrils, made from the secondary dispersed polymer after the blend has undergone strengthening via alignment and stretching of its molecular chains through a mechanical process. Depending upon the method of post-processing during which the matrix polymer is remelted into a continuous phase, the final structure of an MFC can exhibit both quasi-isotropic behaviour as well as varying degrees of anisotropy [15].

Microfibrillar reinforced composites have been reported as having several significant advantages in comparison to some of the more standard polymer composites currently available. These include (i) polymer–polymer reinforcement; (ii) no requirement of mineral additives; (iii) reduced weight in comparison to equivalent glass–fibre composites; (iv) ease of processing; (v) no need for the addition of compatibiliser, and (vi) recyclability and repetition of the process [16].

Microfibrillar reinforced composites do not require the dispersion of a preformed reinforcing into the matrix because their microfibrils are formed in situ, thus avoiding one of the biggest challenges in micro- and nano-composite creation, namely agglomeration of the reinforcing phase. MFCs are also lighter than glass or carbon fibre reinforced composites by virtue of their components' reduced densities. The combination of multiple polymers is considered much easier to break down and recycle than mixed mineral/polymer or thermoset systems.

As well as being easy to manufacture using relatively inexpensive commodity and engineering thermoplastics (such as polyolefins, polyamides and polyesters) on conventional processing equipment, MFCs also display another distinct advantage over similar polymer blends and composites. As mentioned previously, the polymer–polymer bond is generally poor or non-existent in immiscible blends and composites (in the case of non-condensation polymers, unless a high-cost compatibiliser or surface treatment is also used). Interestingly, MFCs from condensation polymers have been reported to exhibit a self-compatibilisation phenomenon that means they do not require these extra additives or treatments to create the desired co-polymeric interface. Additional condensation and transreactions that occur in the melt [17] and the bulk solid state [18] are the causes of this favourable reaction, and thus the usual problems associated with a poor matrix–reinforcement interface are somewhat alleviated [16]. This occurrence is especially significant given reports that the use of a compatibiliser may actually inhibit the formation of high aspect ratio microfibrils by impeding the main mechanism behind their formation, namely the coalescence of adjacent dispersed particles of the reinforcing polymer [19]. Improvements in mechanical properties of blends (including those containing polyolefins with no reactive groups) via transcrystallisation of the matrix polymer on to the surface of the dispersed microfibrils have also been reported for both polyethylene terephthalate (PET)/nylon 12 (PA12) and polypropylene (PP)/PET MFCs [20].

Manufacturing

There are three key requirements that must be satisfied when manufacturing an MFC. First, the constituent polymers must have sufficient drawability to allow the formation of reinforcing fibrils to occur; second, both of the constituent polymers must be able to be processed at a single temperature without the onset of degradation in either polymer; and third, the melting temperature of the reinforcing polymer must exceed that of the matrix polymer by at least 40 °C, to allow fibril retention during matrix consolidation.

Once these requirements have been satisfied, MFCs can be manufactured using standard industrial polymer processing equipment as shown in Fig. 1. This process can be separated into three distinct steps, each vital to the successful creation of a microfibril reinforced composites:

- *Mixing and extrusion*: The matrix and reinforcing polymers are dried and mixed, before being compounded and extruded. This forms an isotropic, continuous blend filament.
- *Drawing and fibrillation*: The blend filament is drawn through pairs of rollers. This step creates highly oriented microfibrils with properties biased predominantly along a linear dimension or symmetry axis [21]. The drawing ratio is defined as the ratio of the linear speeds (S_2/S_1) of the two sets of rollers used to draw the filament and gives an indication as to the amount of alignment imparted to the blend. Next the filament is either collected on a spool (see Fig. 2a) or pelletised.

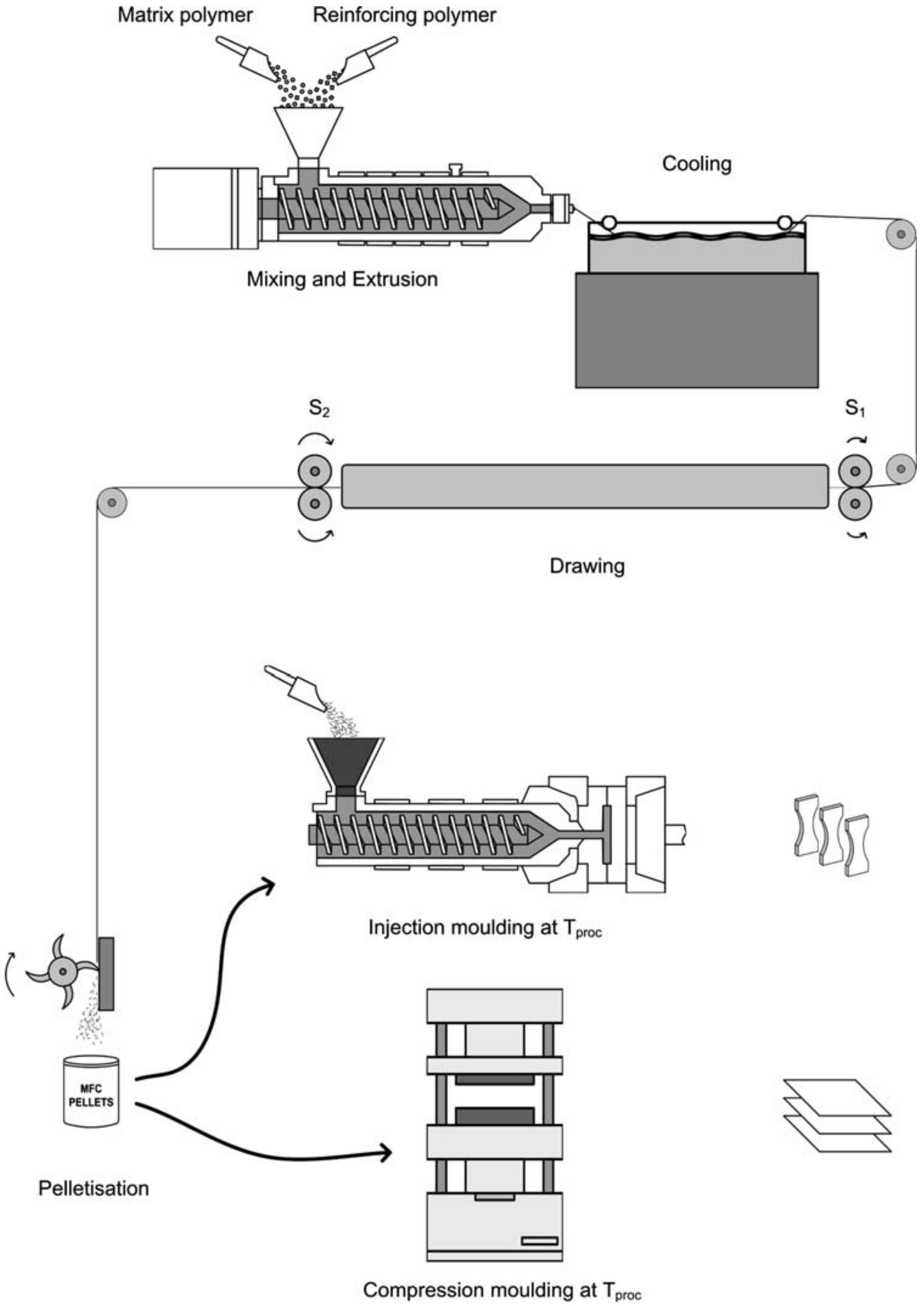

Fig. 1 MFC manufacturing process

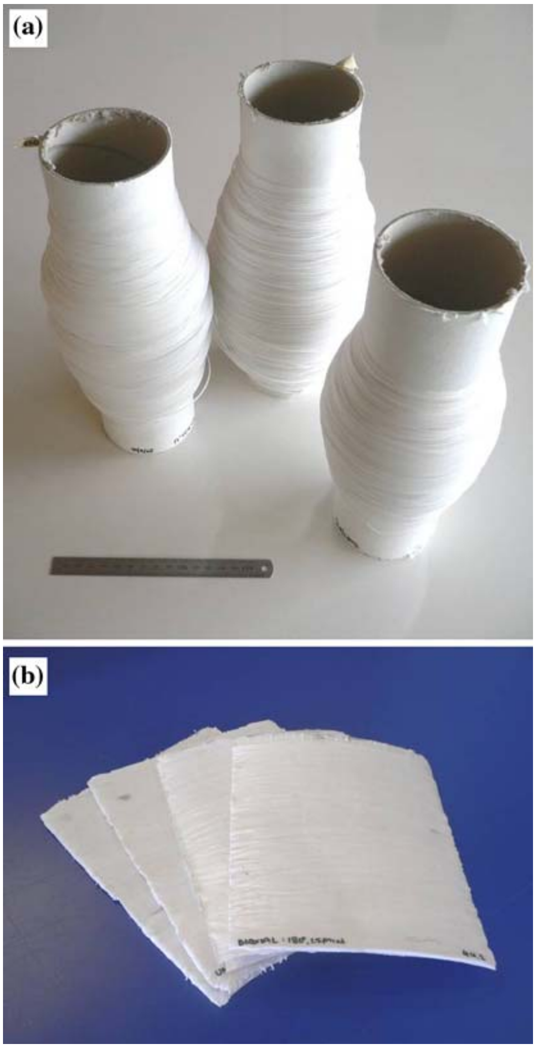

Fig. 2 (**a**) Drawn blend filament is collected on spools before post-processing; (**b**) compression moulded MFC plates

- *Matrix consolidation through post-processing*: The drawn filaments or pellets are formed into a composite at a processing temperature (T_{proc}) that lies between the melting temperatures of the constituent polymers. Control of this temperature is critical to the successful creation of MFCs as it ensures the formation of an isotropic matrix while still retaining the highly oriented reinforcing fibrils. If T_{Proc} is too high the fibrils will melt and the reinforcing effect will be lost. Depending upon the post-processing method, the final composite structure can exhibit either quasi-isotropic or anisotropic tendencies depending on the production method [22]. Compression moulded plates of MFC from PE/PET can be seen in Fig. 2b.

The result of this process is a microfibril reinforced composite material with mechanical properties superior to those of the plain matrix polymer [23]. It should be noted that variations in the MFC manufacturing process do exist. Two different *in-situ* fibril formation techniques can be employed to create the reinforcing microfibrils; cold-drawing of the solidified filament at a temperature below the melting temperature (T_m) of each blend constituent [22–25] or hot-stretching directly from the melt at a temperature above both polymers' glass transition temperatures [26–28]. Cold-drawing generally results in greater molecular alignment within the microfibrils, but hot-stretching can produce much higher draw ratios (although these ratios are not analogous with better molecular orientation). Compatibilisers can also be added to the blend in an attempt to overcome the poor chemical adhesion along the matrix/reinforcement interface that is characteristic of an immiscible and incompatible polymer pairing. Several researchers have added compatibilisers such as maleic anhydride modified PP or ethylene-glycidyl methacrylate to their blends in an attempt to promote stronger interfacial adhesion. Taepaiboon et al. [29] observed that with the use of a compatibiliser (up to 7 wt.%) mechanical results were mixed at the best and that the interfacial adhesion between the matrix and the dispersed phase did not improve much. Use of various quantities of a compatibiliser was also reported by Friedrich et al. [22] to have no noticeable influence on the flexural properties of MFCs from PP/PET, but to limit the formation of high aspect ratio microfibrils by forming a surface layer on the PET spheres and preventing them from coalescing.

Compatibilisers may also hinder nucleation of PE and PP crystallites onto the surface of the PET fibrils (Fig. 3, [30, 31]) and interrupt the formation of transcrystalline layers which have been reported to have a positive effect on the mechanical properties of MFCs because they improve the matrix reinforcement adhesion. It can be seen that close to the PET microfibrils the PE and PP lamellae are not only parallel to each other, but also oriented perpendicular to the microfibril surface. This is in contrast to the bulk polymer, where the lamellae are oriented randomly. The effect of this transcrystalline layer is anticipated to be beneficial to the composite's mechanical properties.

Fibril formation mechanisms and MFC mechanical properties

It is difficult to determine the exact nature of the relationships that exist between various manufacturing parameters used during the MFC production process. Understanding the structural evolution of a blend during compounding and processing is of paramount importance [32]. With a good understanding of the mechanisms shaping the blend morphology during and after extrusion,

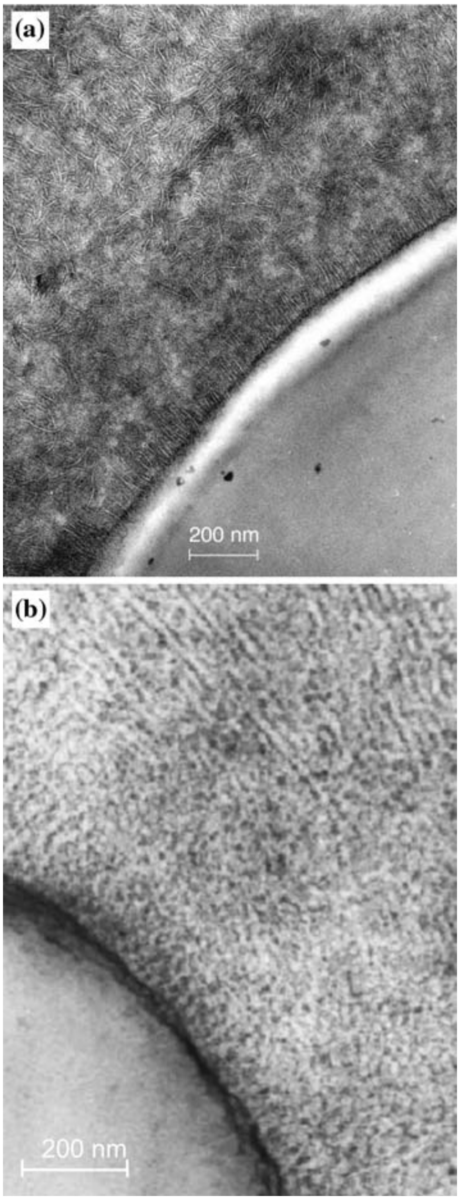

Fig. 3 TEM micrographs of stained thin slices of injection moulded MFC samples of (**a**) an LDPE/PET blend [30]; (**b**) a PP/PET blend [31]

one is better able to manipulate this morphology to achieve a desired outcome, such as specific dispersion shape or particle size.

Morphology during extrusion and drawing

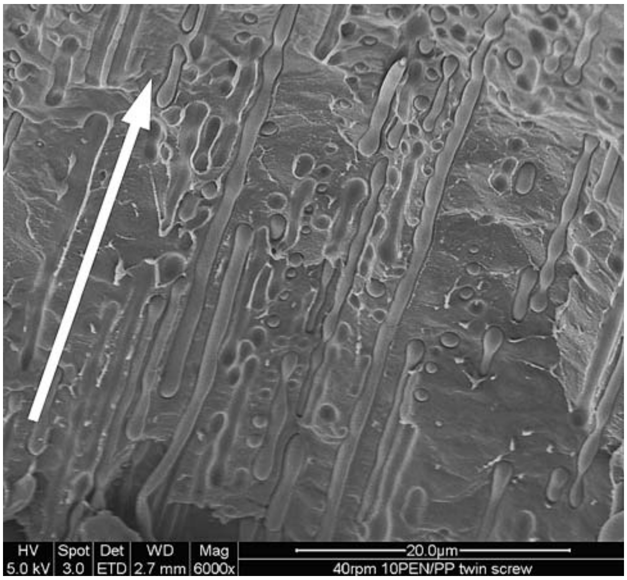

Fig. 4 During coalescence and break-up, particles of the dispersed polymer tend to align in the direction of flow (indicated by the *arrow*). In this case, the blend is 10% PEN in a PP matrix [34]

In an extruded blend, the size and shape of the dispersed phase depend upon the individual viscosities, composition, elasticity, thermal history and interfacial tension of the blend [1]. The structural development of an MFC is initially identical to that of a traditional polymer blend, as they are produced using the same materials, equipment and techniques. The compounding of a polymer blend through an extruder encounters a combination of two distinct flow types [33]:

- *Shear flow*, resulting from a pressure drop along the flow path. The velocity of the fluid perpendicular to the stream varies across the flow, and is lamellar in nature.
- *Elongational flow* (also known as stretching or extensional flow) caused by a tensile or compressive stress acting on the flow stream.

When a spherical drop of a neutrally buoyant material is suspended in another liquid and then subjected to shear or extensional stresses, it initially deforms into an elongated ‘cigar’ shape and then a thread, before interfacial tension between the matrix and the suspended droplet causes the latter to burst into multiple smaller droplets [1]. As illustrated in Fig. 4 from work performed by Leung et al. [34], during blending and extrusion the suspended polymer droplets tend to align themselves parallel to the direction of flow. Blend morphology is also influenced by the behaviour of the dispersed particles in relation to one another, both during and after extrusion. Two dimensionless numbers (the Capillary number κ and the Viscosity ratio λ) are used to predict the occurrence of break-up and coalescence of the distributed polymer in the flow. These phenomena, therefore, depend heavily upon the constituent polymers and their volume fractions.

Extrusion of a blend through the convergent zone of a conical die causes the spheres of the dispersed polymer (Fig. 5a) to elongate into cigars and short fibres (Fig. 5b). Differences between the morphologies of MFCs and other polymer blends do not arise until the fibrillation stage, when the drawing applied to the MFC blend filament causes elongation of the dispersed particles and molecular chain alignment along the axis of tension (Fig. 5c). Lin et al. [35] found that the temperature and speed at which the extrudates are drawn influences the morphology of MFCs, with low temperature drawing leading to the appearance of voids in the material at the matrix/reinforcement interface and increased susceptibility to breakage. They encountered no such problems during high temperature drawing (approaching matrix T_m) although reduced molecular orientation has been reported to occur at elevated temperatures.

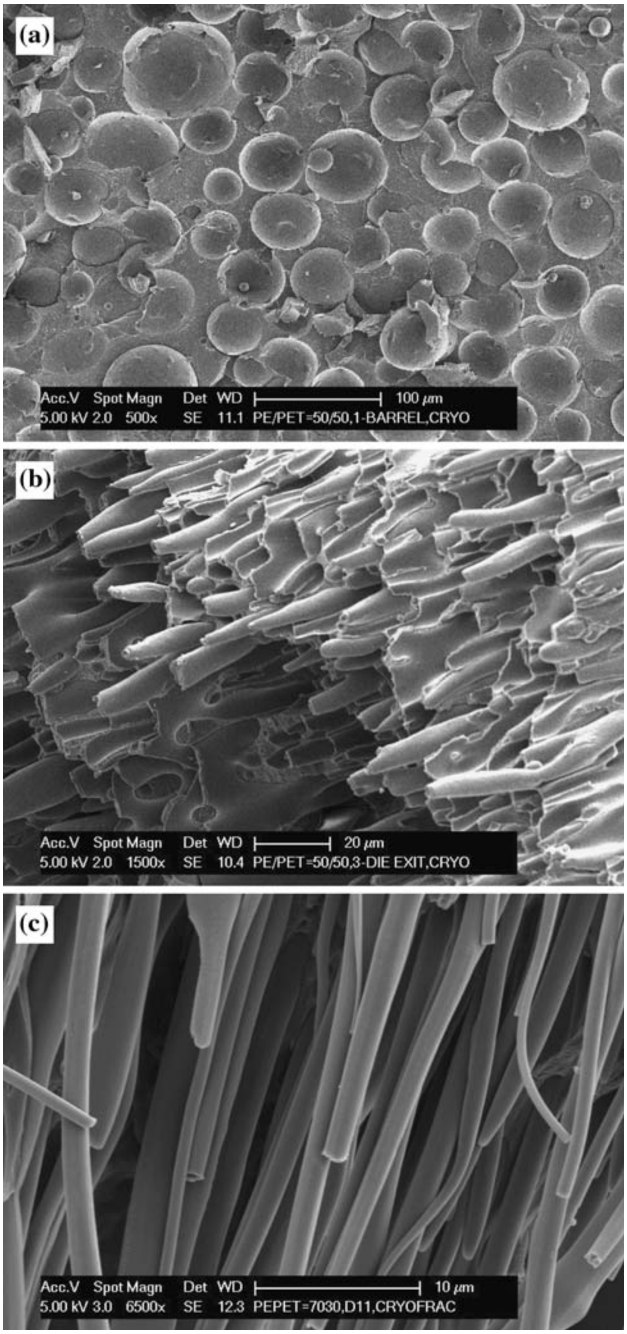

Fig. 5 Blends of PE/PET: (**a**) showing spheres in the extruder; (**b**) after extrusion through a capillary die with cigars and short fibres, and (**c**) with highly oriented microfibrils after cold drawing

Possibly one of the greatest benefits of manufacturing MFCs (as opposed to traditional polymer composites) is the ability to create an even dispersion of reinforcing elements without the need for complex mixing regimes. MFC microfibrils do not agglomerate on the micro-scale level, which is a common problem when trying to disperse micro-/nano-sized fillers in a melt [36].

Mechanical properties of MFCs

Mechanical properties of condensation polymers

Quasi-static mechanical tests of extruded and drawn blends, as well as MFCs based on PET, poly(buthylene

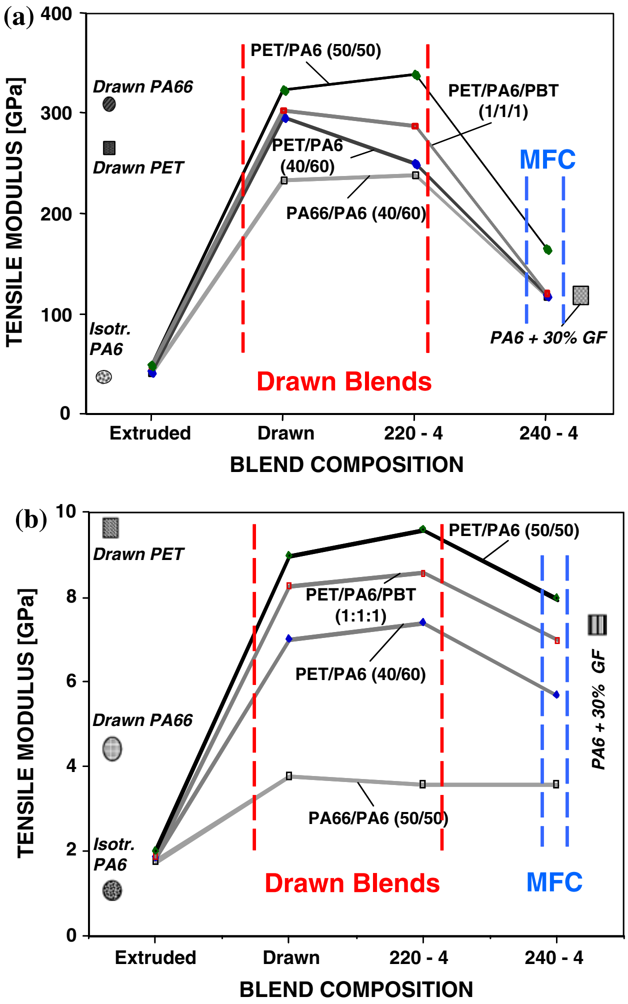

Fig. 6 (**a**) Tensile strength, and (**b**) tensile modulus of extruded and drawn blends as well as blends with MFC structure based on PET, PBT, PA6 and PA66 and MFC with various compositions and of the neat polymers as compared with PA6 reinforced with 30% glass fibres (GF)

terephthalate) (PBT), Nylon 6 (PA6), Nylon 66 (PA66) and of the neat polymers are shown in Fig. 6 [37–40].

The blends comprising PET, PA6, PBT or PA66 at various weight ratios show that the tensile strength σ and tensile modulus E increase drastically after drawing of the as-extruded samples, the latter having properties typical of the undrawn, isotropic matrix (which is PA6). These parameters approach the values of the reinforcing component (PET or PA66) after drawing [38]. As expected, the subsequent isotropisation step results in either slight (for E) or strong (for σ) decrease in mechanical properties, although the material is now converted from a drawn blend to a composite material. In addition, depending on the MFC composition, the mechanical properties at this stage are comparable to a short glass fibre (GF) reinforced matrix (Fig. 6). The σ and E values of the MFC are 30–40% higher than the rule-of-mixture values calculated from the properties of the individual components (e.g., isotropic PA6 and drawn PET [39]), suggesting that a mechanical synergy is occurring between the blend components.

Microfibrillar reinforced composite processed via injection moulding have shown that the tensile strength of the final MFC product can be 50% higher than that of the neat PA6 and only 15% lower than that of 30% GF-reinforced PA6. The modulus is more than double that for neat PA6 and only 35% lower than that of GF-reinforced PA6 [40]. Compression moulded samples comprising three layers of drawn PET/PA6 filaments placed either in parallel $(0)_3$ or cross-plied (0/90/0) have also been tested [39]. Measurements (σ and E) show that maximum σ of the MFC with parallel alignment $(0)_3$ is almost twice as high as that of the cross-plied composite (0/90/0), whereas the E-values of the samples are almost the same. At the same time, compared to neat PA6 and an undrawn PET/PA6 blend, σ has been shown to increase by a factor of almost three [39].

Mechanical properties of non-functionalised polyolefins

Microfibrillar reinforced composites based on polyolefin matrices such as polypropylene (PP) or low density PE (LDPE) and with PET as reinforcement, show the same morphological and structural characteristics as MFCs from condensation polymers. In the case of LDPE, mechanical parameters (σ and E) have been demonstrated as being up to five times higher than the neat matrix values [25]. Mechanical testing by the authors of compression moulded MFCs from linear low density PE (LLDPE)/PET (Fig. 7) with varying types of fibrillar orientation (parallel $(0)_2$, cross-plied (0/90) and random) shows differences in σ and E of over 60 MPa and 1 GPa, respectively, between the principal parallel composite direction and the random or secondary parallel directions. This highlights the enormous contribution to mechanical properties made by the reinforcing fibrils, as well as the differences in isotropy achieved through various preparation techniques.

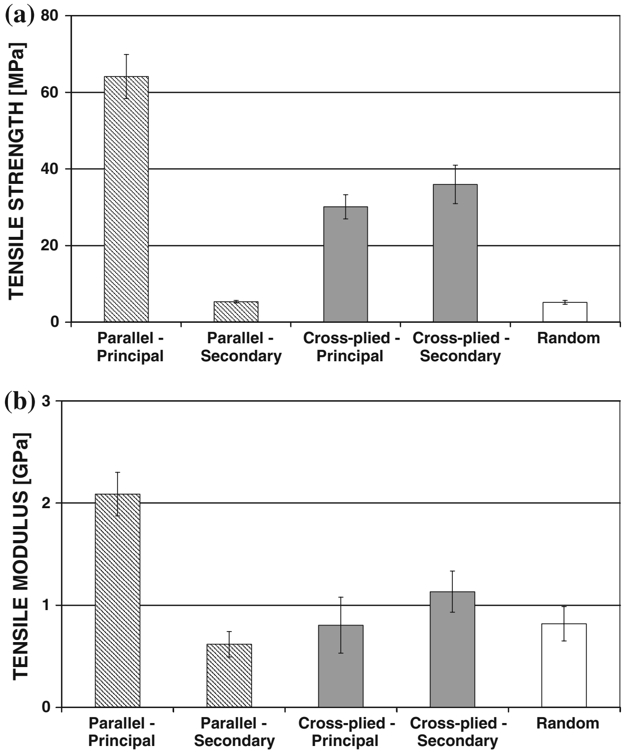

Fig. 7 Tensile properties of MFCs from LLDPE/PET at a ratio of 70/30 wt% for different microfibrillar orientations including parallel, cross-plied and random: (**a**) tensile strength, and (**b**) tensile modulus

Predictions of MFC properties and processing applications

The rule of mixtures (RoM) is commonly used to approximate the tensile modulus, and to a lesser extent the tensile strength and Poisson's ratio of composite materials based on isotropic polymer matrices. It utilises the properties of the constituents in the direction of loading as well as their relative volume fractions, to provide a prediction of the properties of the composite as a whole. It is a fast and simple technique generally leading to accurate results for modulus determination [41], but has several shortcomings as compared to other prediction methods when used for strength prediction, including false assumptions surrounding the component's stress–strain relationship and strain compatibility. When applied to MFCs by Evstatiev et al. [24], RoM calculations indicated that a synergistic effect on mechanical properties had been occurring between the matrix and reinforcing components, with test results exceeding those predicted by RoM. Similar findings were presented in 2004 by Fakirov and his co-authors, who

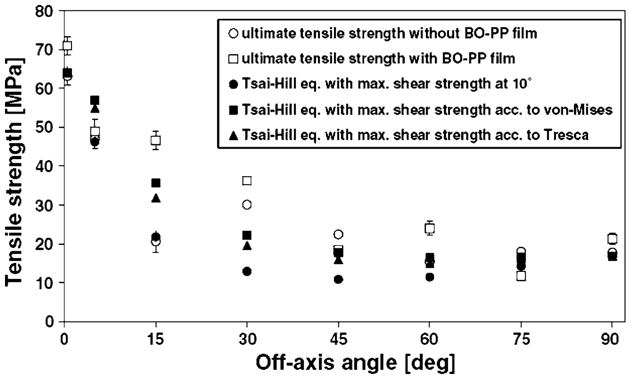

Fig. 8 Actual and predicted values of ultimate tensile strength of MFCs from PP/PET as predicted by the Tsai–Hill equation with various values of maximum shear strength [15]

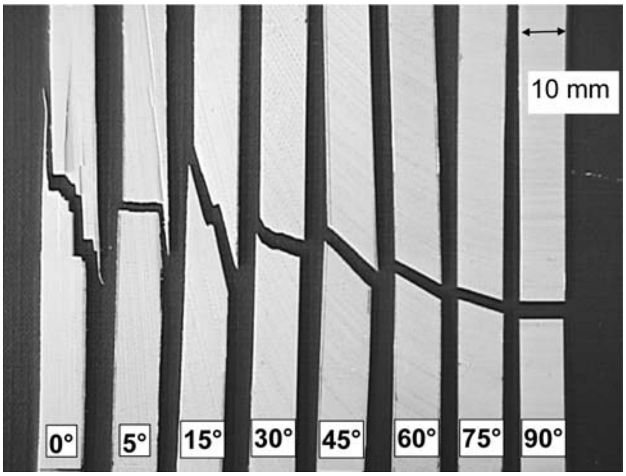

Fig. 9 Fractured MFC specimens of PP/PET used for verifying Tsai–Hill equation [15]

reported mechanical properties as much as 30–40% higher than the calculated RoM values obtained from the isotropic matrix and drawn reinforcement values [23].

Many other models exist for prediction of composite properties, several of which have been applied to MFCs in addition to the RoM. It has been determined that the Tsai–Hill equation (Eq. 1) for the prediction of failure strengths at varying angles of off-axis loading can be applied to fibrillar polymer–polymer composites with relatively good agreement [15] (Fig. 8). This was achieved through the tensile fracture of MFC plates of PP/PET, Fig. 9.

$$\sigma_x = \left[\frac{\cos^2\phi(\cos^2\phi - \sin^2\phi)}{X^2} + \frac{\sin^4\phi}{Y^2} + \frac{\cos^2\phi\sin^2\phi}{S^2}\right]^{-1/2} \tag{1}$$

where σ_x is the tensile strength at a given test angle ϕ, X and Y are the fibre and transverse tensile strengths, respectively, and S is the shear strength. In an extension of this work, injection-moulded samples of another PP/PET blend, with and without compatibiliser, were also tested [19]. Results from these samples were compared to predictions of tensile strengths made for the MFCs using the modified Halpin–Tsai equation proposed by Halpin and Kardos [42]:

$$Z_c = Z_m\left(\frac{1 + A\eta_1 V_f}{1 - \psi\eta_1 V_f}\right) \tag{2}$$

where

$$A = 2\frac{l}{d} \tag{3}$$

$$\eta_1 = \frac{\frac{Z_f}{Z_m} - 1}{\frac{Z_f}{Z_m} + A} \tag{4}$$

and

$$\psi = 1 + \left(\frac{1 - \phi_{\max}}{\phi_{\max}^2}\right)V_f \tag{5}$$

Z_c, Z_m and Z_f represent the Young's modulus or tensile strengths of the composite, matrix and fibre, respectively, A is twice the fibre aspect ratio (l and d are the fibre length and diameter, respectively), η_1 accounts for the relative moduli of the fibre and matrix, V_f is the fibre volume fraction, ψ depends upon the particle packing fraction and $\phi_{\max}$ is the maximum packing fraction of the reinforcement.

While suitable agreement has been achieved for non-compatibilised MFCs, the same cannot not be said for those containing 1–9 wt.% compatibiliser. The suitability of using the Halpin–Tsai equation for injection moulded MFCs has also been called into question by Li et al. [27] after poor agreement between predicted and experimental results for slit-drawn PE/PET specimens. The reason can be attributed to the fact that the properties of the bulk polymers (especially the reinforcing PET) depend so heavily upon the degrees of drawing and crystallinity applied to each individual polymer that the Halpin–Tsai equation cannot achieve the same degree of accuracy from the initial 'bulk material' values normally achieved for more consistent, homogeneous materials such as glass or carbon fibres.

The characterisation of various properties or the MFC manufacturing process has generally been attempted in a somewhat disjointed manner. To address this issue, the authors are currently at the final stages of a complete experimental design investigating the influence of most important manufacturing parameters on a range of mechanical and barrier properties of polyolefin-matrix MFCs using the well known 'Taguchi' statistical analysis method. Supplementary to this, papers detailing further impressive results of injection moulded MFCs [43] as well as the mixed results from work regarding the application of these materials to rotational moulding have also been published recently [44, 45].

Oxygen barrier properties

The potential for MFCs to significantly improve the oxygen barrier properties of low cost plastics such as PE without the need for complicated and expensive co-extrusion procedures, has been thoroughly investigated [46].

Differences in the gas permeabilities of plastics occur because of the enormous variations in molecular structure and chain distribution possible between different types and grades of polymers, as well as due to the different sizes and shapes of penetrant molecules. Blend morphology in multi-component systems influences the diffusion paths available to these molecules, as do the degree of branching and cross-linking, the structure of the monomer units and the level of free volume present in the polymer [47, 48]. Barrier properties are also influenced by crystallinity as amorphous regions tend to be easier for molecules to permeate through compared to tightly packed crystalline regions [49].

Several common techniques used to improve the barrier properties of a polymer film include: (i) combining multiple polymer layers in a single film; (ii) coating low barrier polymers with higher barrier materials; and (iii) filling low barrier polymers with inorganic platelets or high barrier polymer lamellae, spheres or fibres [50]. For this last technique, the choice of filler influences the mechanical (as well as barrier) properties of the polymer and thus has the potential to provide multiple benefits. However, these benefits depend upon several factors, including the shape and size of the reinforcing phase and its orientation relative to the direction of permeation.

An experimental design method has been used by the current authors to examine the effects of several of the MFC manufacturing parameters on the final barrier

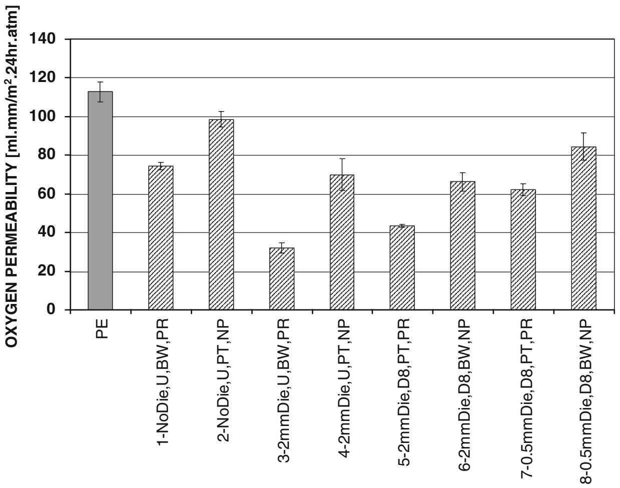

Fig. 10 Oxygen permeability of MFC films from LLDPE/PET = 70/30 (wt.%). Films are named 1–8, followed by the extrusion die diameter, drawing ratio, fibril orientation and cooling conditions, where U = undrawn, D8 = draw ratio of 8, BW = biaxially wrapped, PT = pelletised, PR = pressure cooled, and NP = no pressure cooled. For full experimental details refer to [46]

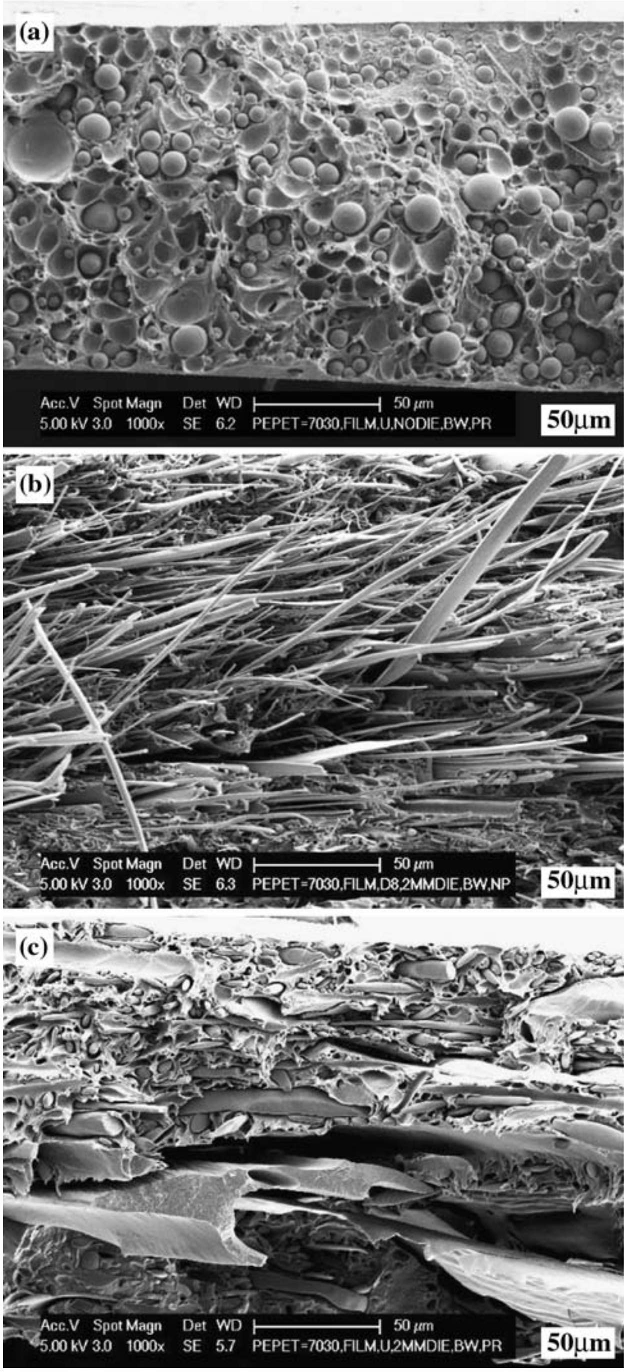

Fig. 11 SEM images of the through-thickness microstructure of LLDPE films containing 30% PET, showing a variety of reinforcing morphologies: (**a**) spheres; (**b**) fibrils, and (**c**) plates

properties of the composite films. LLDPE/PET films were manufactured at a ratio of 70/30 (wt.%) using various combinations of processing conditions (die diameter and drawing ratio), cooling conditions and microfibril orientation. The full details of the experimental design and film production parameters are given in [46]. Oxygen permeability results, plotted in Fig. 10, show that a plain PE film has three times higher oxygen permeability compared to selected MFC films. Morphological analysis using SEM has, unsurprisingly, shown that films reinforced with spheres of PET (Fig. 11a) possess much poorer barrier qualities than those reinforced with PET microfibrils (Fig. 11b). A film that contains microfibrils combined with plates of PET has even lower permeability than microfibril-only films because of its higher effective gas blocking area (Fig. 11c).

The size of the die aperture used during extrusion also appears to have a much greater influence on oxygen permeability than the level of drawing applied to the blend, because it determines the shape and size of the reinforcement rather than its molecular structure. Leaving films in the press during cooling also reduces permeability because it slows down the cooling rate and hence increases the crystalline content of the film. Orientation of the filament during film preparation has little effect because it does not change the in-plane alignment of the reinforcement and so does not alter the gas tortuosity significantly.

Potential applications of MFCs

Food packaging

One potential application for MFC films that draws upon multiple performance demands is that of a protective barrier film such as those used in the packaging of food. Commodity polymers have proven themselves very well suited to this role, ideal for creating inexpensive containers and films that are easy to produce in large quantities. Unfortunately, these polymers have varying levels of effectiveness when it comes to one of the biggest factors contributing to the degradation of many food products—the permeation of gases or liquids (such as air, oxygen, nitrogen, carbon dioxide or water vapour) between the product and the environment. In particular, PE exhibits extremely poor oxygen barrier properties [51, 52].

A range of MFC films have been manufactured from blends of LLDPE/PET at the ratio of 70/30% (by wt.) using melt blending, extrusion, drawing and compression moulding processes (refer to [46] for full manufacturing details). With relation to the oxygen permeability results of Fig. 10, the mechanical properties of the same group of barrier films can be seen in Fig. 12. It is evident that undrawn films (#1–4) exhibit poor mechanical properties compared to drawn films, but in several cases are still superior to the unreinforced LLDPE films. Improvements of up to 200% for tensile modulus and 75% for tensile strength are realised by using the MFC process to reinforce the PE matrix with well oriented, high aspect ratio microfibrils (#5–8). Consideration of mechanical and permeation results confirms that MFCs can consistently outperform plain LLDPE films in both of these areas.

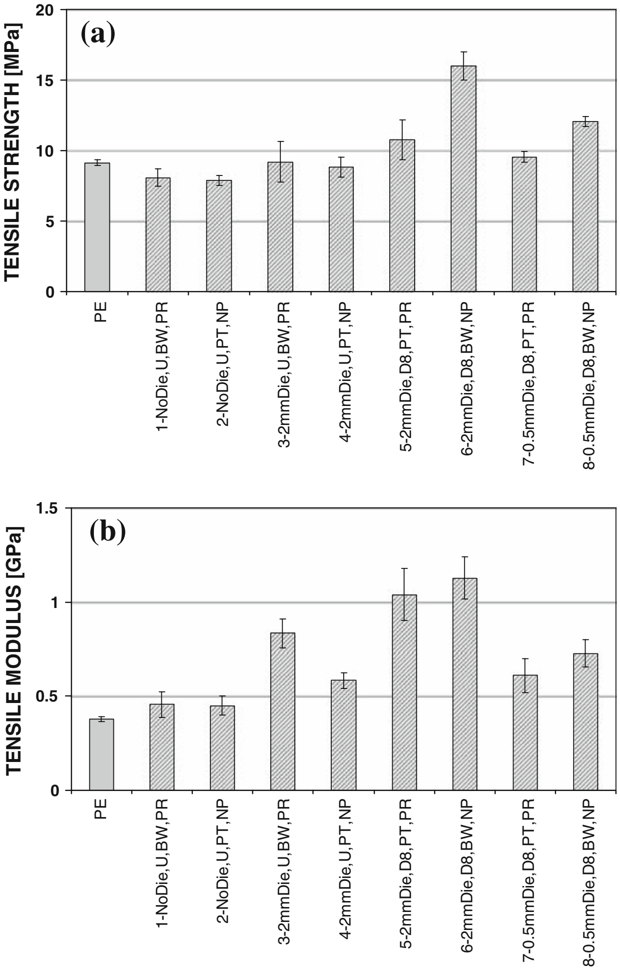

Fig. 12 Tensile properties of LLDPE and MFCs from LLDPE/PET = 70/30 (wt.%): (**a**) tensile strength, and (**b**) tensile modulus. Films are named 1–8, followed by the extrusion die diameter, drawing ratio, fibril orientation and cooling conditions, where U = undrawn, D8 = draw ratio of 8, BW = biaxially wrapped, PT = pelletised, PR = pressure cooled, and NP = no pressure cooled. For full experimental details refer to [46]

These results indicate that there is much potential for MFC films to be developed into packaging materials suitable for applications in which PE is currently the material of choice. Permeation results have shown that significant barrier improvements can be attained with both an extruded blend and a drawn microfibrillar structure, but that drawing of the blend is paramount if significant increases in tensile strength and modulus are also desired.

Scaffolding

The MFC concept has also recently been applied in the biomedical world, more specifically in the area of tissue engineering. As a new technology for the manufacturing of nano- and microfibrils, the MFC production process can help meet the stringent demands of regenerative medicine, and specifically extend the current options of stem cell bioengineering. The use of the MFC process to produce 'scaffolds' of microfibrils from appropriate biodegradable polymers can provide structures capable of sustaining the growth of living cells.

This quickly developing field uses tissue-specific cells in a three-dimensional arrangement, provided by a scaffolding material, to return functionality to an organ [53]. The purpose of scaffolding is usually to (i) support differentiated cell function and growth [54]; (ii) transport cells, cell nutrients and biochemical factors, and (iii) provide mechanical support to maintain a space for tissue to form [55].

Advantages of the fibrillar and highly porous matrices from MFCs derived from micro- and nanofibrils include their microstructural adaptability, dedicated bioactive characteristics, fine-tuned degradability and the fact that the synthetic component is produced without any contact with organic solvents or high-temperature treatments. The scaffolding matrix should be biocompatible, not induce a tissue response in the host, and be completely absorbable leaving a totally natural tissue replacement following degradation of the polymer.

Polymers in the group of polyesters, specifically the family of poly(lactic acid) (PLA) and poly(glycolic acid) (PGA) and copolymers of lactic and glycolic acids (PLGAs), as well as poly(β-hydroxybutyric acid) (PHB) most closely fulfilled the criteria outlined above including biocompatibility, processability, and controlled degradation [54]. In addition to the required chemical properties, physical properties such as high specific surface area for cell attachment are essential. This can be achieved using fibrillar and/or porous materials.

Many current scaffold production methods involve the use of harmful and expensive organic solvents that may be trapped in scaffolds. They are harmful to cells and reduce their ability to form new tissues. As indicated by Mikos [56], the use of solvents is the major factor that often precludes the use of scaffolds during surgery.

It should be noted that the possibility for creation and isolation of microfibrils via selective polymer dissolving from MFCs is well proven [20, 57, 58]. The diameters of microfibrils depend on the sizes of the preceding particles and can be controlled somewhat by varying the melt blending and drawing conditions. In this way nanofibrillar composites (NFC) have recently been prepared, with reinforcing fibrils between 50 and 150 nm in diameter [59].

Another intention in the development of this work has been to avoid the use of toxic organic solvents that can have a negative influence on the seeded living cells as outlined above [56]. The best solution to this is to use water as a solvent. For this reason, a water soluble blend partner of PLA was selected, namely poly(vinyl alcohol) (PVA).

The MFC concept was first applied to preparation of microfibrillar biohybrid matrices via (i) coating the long microfibrils with collagen I or collagen I/glucosaminoglycan, and (ii) reinforcement of microfibrillised collagen (or collagen/glucosaminoglycan cofibrils, respectively) with short PLA microfibrils. This was followed by moulding of the desired part with eventual fixation or conditioning.

More recently, the use of water soluble PVA with PLA to produce fibrillar composites has been reconfirmed [60]. An interesting finding from the scanning micrographs at high magnifications was that the PLA micro- and/or nanofibrils were interconnected, forming a three-dimensional network (Fig. 13a). Such a spatial arrangement of

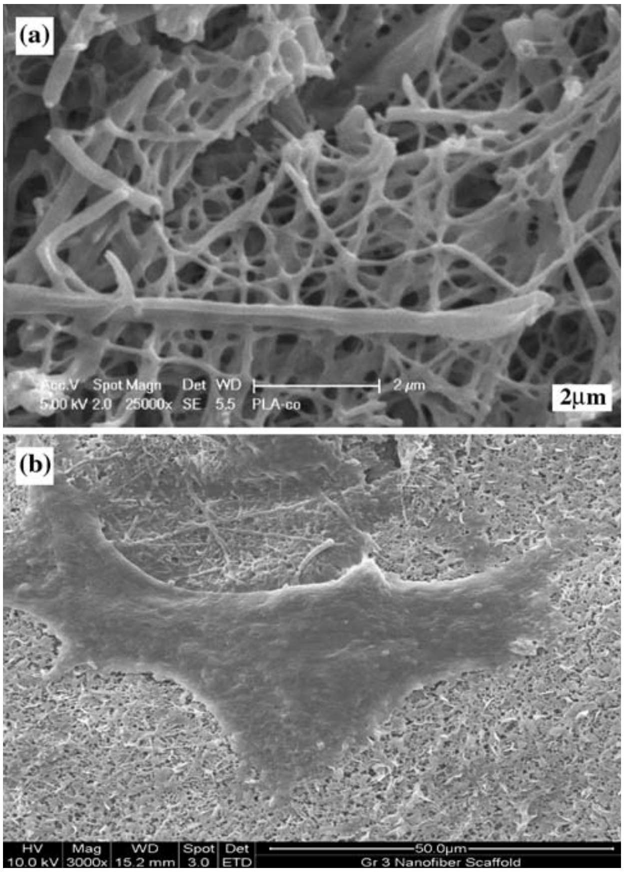

Fig. 13 Microfibrillar scaffolds from MFC: (**a**) displaying a three dimensional network, and (**b**) with living cells forming

microfibrils results in the formation of extremely porous material where the pores have sizes in the nano range.

The results of the biomedical testing with living cells are also shown in Fig. 13b. The living cells attach rather well to the scaffold surface, proliferate and grow further forming continuous tissue. The final products have a nanoporous structure, which makes them highly absorbent to nutrition solutions for the cells. The same nanoporous structures makes them attractive candidates as carriers for controlled drug delivery.

Concluding remarks

The MFC concept seems to be a powerful but simple approach for the processing of polymer blends and the manufacturing of polymeric materials with environment-friendly properties, insofar as no mineral reinforcements or additives are used. These fibrillar composites also have the advantage of featuring an extremely homogeneous reinforcement distribution. The mechanical properties of MFCs show much promise in being able to meet and exceed those of the constituent matrix materials, in some cases improving the tensile strength and modulus of a polymer by as much as several hundred percent.

Several potential applications exist for MFCs in the near future, including roles as reduced or controlled permeability packaging materials and as tissue engineering scaffolds. Composite films based on LLDPE matrices have shown excellent improvements in oxygen barrier properties as well as good improvements in mechanical properties. Preliminary tests of these scaffolding samples in biomedical conditions demonstrate that it is possible to successfully create highly porous scaffolds from extracted nanofibrils of PLA, and that living cells proliferate successfully on these scaffolds and form continuous living tissue.

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