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Micro-fibrillar fiber of bicomponent polymer blends: Traditional paradigm with modern approach

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Abstract

This review article focuses on the micro-fibrillar fiber origin, its importance and its traditional methods of preparation. Further the different factors which effect the properties of microfiber are being summarized over here. The effect of viscosity ratio, compatibilzer role as constituents are highlighted in the view to point out there importance in microfiber formation. Also the two most common and easily controllable processing factors: draw ratio and drawing temperature are studied over here which governs the structure, crystallinity and conductivity of the fiber. The review covers the CNTs based microfibers being researched so far describing the factors effecting the properties of the fiber and hence correlating the traditional method of fiber formation with incorporation of modern concept of nanotechnology to form high performance micro-fibrillar fiber. Copyright © 2018 VBRI Press.

Keywords: Microfiber, polymer blends, melt spun, MWCNTs.

Introduction

Micro-fibrillar fiber: what holds its origin; what is it and what is its importance as well as how it could utilize the essence of nanoworld? These are the major questions which would be answered in different and detailed section of this review.

Concise view on long journey of polymeric science

Polymer world has grown with its fastest pace in the twentieth century after the rising concept of macromolecules and with its utilization on industrial level. Emil Fischer the great Nobel Laureate 1902, claimed that there exist no molecules above the molecular weight 5000. He was Hermann Staudinger (Chemistry Nobel prize 1953) the one to bring up the concept of macromolecules and terminology of polymer. DuPont Company with its revolutionary thought transformed itself from a gun powder factory of 1900 to a leading world producer of fiber for the 20th century.

After the Ziegler Natta Catalyst (Nobel Prize 1965) the utilization of polymer increased with no barrier. Isotactic polypropylene, high performance fibers of polyethylene took up the material world. The thirst and growth of new materials increased day to day until the last two decades when polymeric world faced a saturation and number of synthetically commercially manufactured polymers remains almost constant.

However the quest of improved and new polymeric material had already became the basic necessity of growing era. To pace this situation experience recalled itself and stated that now the satisfaction could be brought not by synthesizing newer unknown polymers but by proper modification of commercialized polymers.

Polymer-Polymer Composite (PPC)

The above mentioned contemplation gave thought of blending, reinforcement, drawing, and controlling the crystallization process, etc. Such physical process could give improvement in mechanical properties on comparison to traditional polymers. However, the partners in most of the polymer blends are thermodynamically immiscible and technologically incompatible. As a result, during processing a large variety of shapes of the dispersed phase can be formed, e.g. spheres or ellipsoids, fibrils or plate. Which of these is actually formed depends on the weight ratio of the blend components, their chemical structure, their properties, and the processing conditions. It is well known that shape and size of the dispersed phase strongly affect the properties of the final polymer blend. Processing of an incompatible polymer pair in which the dispersed phase forms in situ reinforced fibers is the preferable way to achieve the highest mechanical properties.

Reinforcing composites with traditional fibers like glass or carbon was also promising as it give excellent mechanical properties but the issue of recyclability and its environment impact became the new challenge to be dealt **[1]**. Here arises the two major issues: first being the processing problem due to incompatibility and other the recyclability.

Polymer polymer composite (PPC) came out as a broad term to solve these both issues. The problem of recyclability and environmental related impact could be lowered as these could be easily recycled and the reinforcements could be recreated directly in the blends **[2]**. Thermodynamic incompatibility and processing issue as stated above; was another major question to be answered. One method of it was utilization of in situ composite formation using Thermotropic Liquid crystalline polymer (TLCP). These blends are often referred to as in situ composites because in elongation flow fields that occur in polymer processing operations, e.g. the advancing front in injection molding, the LCP phase will elongate into oriented fibrils that reinforce the thermoplastic. However the LCPs are often too expensive for general engineering applications. On the other hand, there are considerable supplies of engineering plastics in the form of post-consumer scraps, which are a low cost source of raw materials for forming polymer blends. But, opposite to LCPs, the molecules of common thermoplastics relax during melt processing; therefore a good molecular orientation is almost impossible.

Micro-fibrillar fiber

A new type of processing route, the so called Micro-fibrillar fiber / micro-fibrillar reinforced composite (MFC) concept was created about 20 years ago. Unlike classical macro-composite (e.g. glass fiber reinforced one) or in situ composite (TLCP macromolecules), MFC are micro-fibrils of fibril chains which in turn are created during MFC manufacturing. The quality of adhesion at interface of matrix-reinforcement and the aspect ratio of reinforcing particles governs the mechanical performance of composite. Creating PPC with the concept of MFC came out as one of the most promising solution since polymers are much closer chemically to each other than their mineral counterpart and hence better adhesion property could be expected.

Another step involved in MFC allow the isolation of neat polymer micro-fibril and nano-fibrils out of it which has given new addition to the field of PPC. These isolated micro-fibrils itself could as fillers since like other micro/nanofillers they also exhibit distinguished properties than their larger counter parts viz are increased strength which help them to be a stronger reinforcing agent, increased aspect ratio and moreover-all unique manufacturing process overcomes the dispersion problem that causes many other nanofillers to fail to meet upto there expectations **[3]**. Single Polymer Composite (SPC) is another new sub-branch of PPC rather MFC; which utilises one component system i.e. similar polymer act as matrix and as reinforcing fiber to further improve the adhesion and recyclability problem.

In addition to all this evolution of nanofillers with the field of nanotechnology again gave us an opportunity to broaden the field of PPC and MFC. Due to the growth of nanofillers like CNTs, graphene who itself have great mechanical strength and conductivity; involvement of nanotechnology in PPC and more overall in fiber science became a hot topic of research. More than 35,000 papers on the topic of carbon nanotubes and over 1800 of these papers addressing the issue of carbon nanotube fiber or carbon nanotube containing fiber got published in just a decade from its origin in 1991.

Again the concept of polymer nanocomposite standing on the ground that using 1-5% nanofiller instead of 30-40% will possibly give magnitudes of improvement over traditional composites faced major challenges due to (i) poor dispersion (ii) poor interfacial load transfer (iii) processing inabilities (iv) bulk production (v) poor alignment.

Taking all these views MFC became as a Connecting link between the traditional concept and modern approach. MFC structure incorporated with nanofillers (mainly in its core) rose as another branch of study in material science. It is supposed that such structures and composites could allow full utilization of properties of polymers along with nanofillers keeping in mind the adhesion, dispersion and recyclability issues. Also further isolation of micro-fibrils with nanofillers deeply situated inside its core can again improve its properties and usage.

This review/book chapter will focus on the structure of MFCs and its different processing route. Further giving emphasis on melt spinning (most traditional process) a detail study with examples of melt spun MFCs and MFC reinforced with nanofillers especially Carbon Nanotubes would be summarized. More precisely it will discuss on different factors of processing affecting different properties of this relatively new class of Micro-fibrillar fiber reinforced with Carbon nanotubes.

Traditional manufacturing process

This section mainly deals with the different traditional techniques for the processing of MFC. Before going for the processing technique the structure of MFC should be clearly dealt out. Further different processing parameters and constituents properties affect differently on overall properties of microfiber which are whole solely summarized over here.

Structure of MFC

Minutely observing the structure of MFC, it could be stated as one of the type of Bicomponent fiber. For this one should understand the definition and different types of Bicomponent Fiber. By definition Bi-component fiber is a polyblend consisting of two components divided into two relatively distinct regions with the cross section extending along the fiber length **[4]**.

Or in other words Bi component fibers consist of two or more polymer components within the same filament, with each component existing separately. Dupont introduced the first commercial bicomponent application in the mid-1960s. In the 1970s, various bi-component fibers began to be made in Asia, notably in Japan. Very complex and expensive spin packs apparently were used in the manufacturing process. These techniques were found to be technically unsatisfactory and excessively expensive. Later in 1989, a novel approach was developed using thin flat plates with holes and grooves to route the polymers. This process was very flexible as well as quite price effective **[5]** and then hence its study took a pace.

The main objective of producing Bi-component fibers is to exploit capabilities not existing in either polymer alone. By this technique, it is possible to produce fibers of any cross sectional shape or geometry that can be imagined. Bi-component fibers are commonly classified by their fiber cross-section structures as side-by-side, sheath-core, islands-in-the-sea and citrus fibers or segmented-pie cross-section types as shown in **Fig. 1**. **[6]**

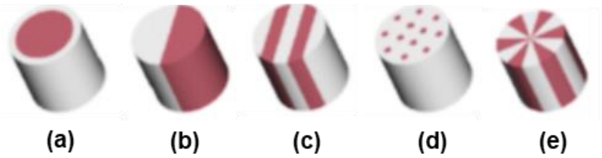

Fig. 1. Cross sections of bicomponent fibers: (a) sheath-core, (b) side-by-side, (c) layer-by-layer, (d) islands-in-the-sea, and (e) segmented pie [11].

Conventional method of manufacturing

Basic flow chart for formation of fiber from polymer follows the steps **(Fig. 2)**:

Fig. 2. Steps showing formation of fiber from polymer.

First Step: Polymer to Fiber Conversion via Spinning

Two major routes could be applied for fiber formation

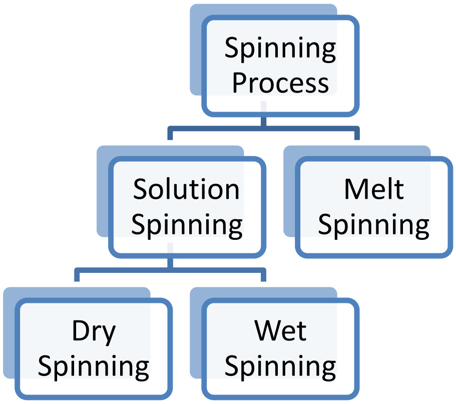

Fig. 3. Routes of fiber forming Spinning Techniques.

Post spinning operation

The as spun fibers formed through first step of spinning probably don't have the required properties. In order to attain desired properties fibers are post drawn which allow the alignment of molecules in the long axis direction which result in attaining higher crysttanility along with orientation **(Fig. 3)**.

To stabilize the fibers drawn fibers are heat settled for making it dimensionally more stable which occurs due to the post-crystallization and stress relaxation.

Melt spinning

For producing filaments within fibers melt spinning is utilized. But the condition for melt spinning says that polymer should melt without degradation. Some examples of such polymers are nylon-6, nylon 66, poly (ethylene terephthalate) and poly (propylene). A representative schematic **Fig. 4** & **Fig. 5** shows the different step of formation of microfiber in the polymer matrix.

Melt spinning uses the heat to melt the polymer to a viscosity suitable for the extrusion through the spinneret. As the name indicates the chips of fibers are melted and extruded through the spinneret to obtain the fibers. Polymer chips obtained from previously reacted chemical combinations are melted and then pumped through a spinneret in an air chamber. The extruded stream cool and solidify into continuous filaments and are then drawn out of the chamber twisted and/or processed further and subsequently wound onto the spools **[13]**.

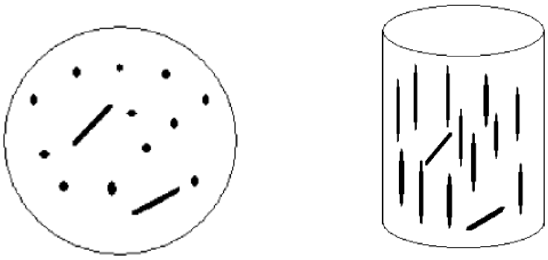

Fig. 4. Schematic for Transverse and lateral sections of MFCs.

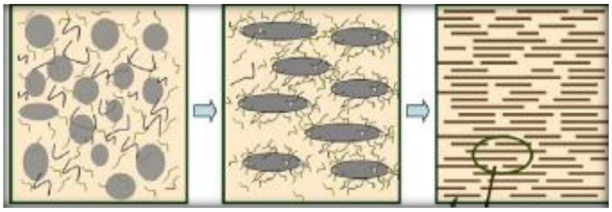

Fig. 5. Schematic diagram showing formation of MFC with major and minor phase along with fillers (CNTs).

The CNT composite fiber by melt spinning

Haggenmueller *et al.* was the one to do earliest study on polymer-carbon nanotube melt processing study **[14]**. Main target of the melt-spun fibers is enhancement of mechanical properties and electrical conductivity but the challenge is the dispersion of CNTs in the polymer matrix. As the dispersion of CNT in polymer melt is much more difficult than in solution, many kinds of methods have been investigated to enhance the dispersion.

Meng *et al.* **[15]** incorporated multi-wall carbon nanotubes (MWNT) into the shape memory polyurethane fiber by in-situ polymerization with treatment of MWNT in concentrated nitric acid and sulfuric acid. They demonstrated that through the mechanical stirring, ultrasonic vibration, melt blending, extrusion and melt spinning, the MWNT were distributed homogenously and preferentially aligned along the fiber-axial direction. Shen *et al.* **[16]** tried another way by premixing CNT with poly (ethylene terephthalate) (PET) in a solvent, dried it and then carried out melt spinning reporting an increase in the tensile strength of the composite fibers by 36.9 % (from 4.45 to 6.09 cN/dtex), and the tensile modulus by 41.2 % (from 80.7 to 113.9 cN/dtex) with addition of 0.02 wt% of acid treated MWNT.

Shape memory fiber with higher shape recovery ratio and force was reported by Meng *et al.* **[17]** They suggested that the aligned MWNTs provided higher shape recovery ratio and shape recovery force because the aligned MWNTs could help storing and releasing the internal elastic energy during stretching and shape recovering. It was also compared with pure shape memory polymer (SMP) (polyurethane is the SMP used in this study) fiber, SMP-MWNT fibers recovered the original length more quickly providing the possibility of producing more sensitive smart instruments.

Solution spinning

Another technique similar in principle to melt spinning is solution spinning. The only difference lies that the melting point of the polymer is depressed to below the room temperature by adding a solvent where finally the solvent have to be removed either by coagulation or evaporation for allowing solidification of fiber. Thus similar to melt spinning solution spinning involves heat transfer along with one-way or two-way mass transfer.

However, there are principally two types of solution spinning methods

a) wet spinning

b) dry spinning

The types of solution spinning differ in the process of extrusion, where a polymer is dissolved in a suitable solvent and in wet spinning they are extruded inside a coagulation bath containing a non-solvent while in dry spinning extruded into a heated chamber of air. Another subtype is dry-jet wet spinning where the polymer solution is extruded in the air but eventually taken into a coagulation bath **[13]**.

The CNT composite fiber by solution spinning

Since de-agglomeration of CNT play important role in fiber formation of CNT based composite fiber, so solution processing has been extensively used to prepare these fibers. Major benefit is that agitation of the nanotube powder in a solvent facilitates nanotube dispersion. In general, agitation is provided by magnetic stirring, shear mixing, reflux, or most commonly, ultrasonication. The most effective and common method is sonication which can be done in two ways: bath sonication which is mild and high-power sonication through probe **[18]**.

Enhanced CNT alignment in formed fiber was shown by Vigolo by injecting CNT solution into a rotating bath of poly (vinyl alcohol) (PVA)/water solution **[18]**. Miaudet demonstrated that these fibers can be drawn at above the glass transition temperatures of PVA, resulting in improved nanotube alignment and polymer crystallinity **[19]**.

The ability to prepare super-strong fibers by using poly (p-phenylene benzobisoxazole) (PBO) was explained by Kumar *et al.* **[20]**. They also suggested that polyacrylonitrile (PAN)/ single-wall carbon nanotube (SWNT) composite fibers can be used as a precursor for carbon fibers with enhanced mechanical properties **[21]**. Carbonized PAN/SWNT (1wt% SWNT) fibers exhibited 64% higher tensile strength and 49% higher tensile modulus than the carbonized control PAN fiber. High-resolution transmission electron microscopy (HR-TEM) and Raman spectroscopy evidenced the graphitic structure formation in the vicinity of SWNT at a relatively low carbonization temperature (~1100^{o}C). Electrically conductive fibers are also one of major applications of CNT composite fibers [134]. Recently fibers were also made from the solution of natural polymers such as DNA, chitosan, and gelatin for application as biomaterials such as artificial muscles **[22]**.

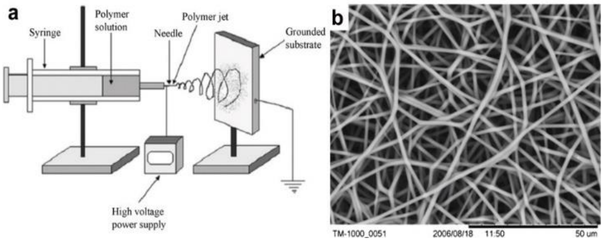

Fig. 6. (a) Schematic of a standard electro spinning setup and (b) Electro spun nano fibers [23].

Electro spinning

Formation of nanofibers from solution is now more commonly formed via a newer method of electro-spinning. Electrospinning has emerged to be a simple, elegant and scalable technique to fabricate polymeric nanofibers. Pure polymers as well as blends and composites of both natural and synthetics have been successfully electrospun into nanofiber matrices **(Fig. 6)**. Electrospun nanofiber matrices show morphological similarities to the natural extra-cellular matrix (ECM), characterized by ultrafine continuous fibers, high surface-to-volume ratio, high porosity and variable pore-size distribution **[23]**. Electrospinning was first patented in the US in 1902; however, the process was largely forgotten until the 1990s. With interest in the field of nanoscience and nanotechnology, researchers began new investigations of nanofiber production using electrospinning and now Electro-spinning is not only the focus of intense academic investigation; the technique is already being applied in many technological areas **[24-25]**.

The CNT composite fiber by electro spinning

Electro-spinning was firdtly described as a method to fabricate polymer/CNT composite fibers and yarns by Ka *et al.* **[26]**. Through this techniques nanometers range (10 nm -1 µm) fibers could be formed easily. Sen formed fiber based membranes by electro-spinning solution of SWNT dispersed in either polystyrene or polyurethane **[27]**. Electro-spun composite fibers based on polycarbonate with MWNT was prepared by Kim **[28]**. They reported the membrane composed of the composite fibers exhibited strong and tough properties **(Table 1)**. They suggested that the results may provide a feasible consideration of such electro-spun composite fibers for use as the reinforcing elements in a polymer based composite of a new kind.

Table 1. Some important contribution in CNT-Polymer composite fiber.

Polymer	CNT	Focus of the research	Reference	Year
PVA	MWCNT	Flexibility humidity sensing material	[31]	2016
PAN	MWCNT	3D porous monolith with high electrical and thermal conductivity	[32]	2016
PMMA	CNT	Electromagnetic inference of shielding properties of polymer with high electrical resistance	[33]	2015
PIA	CNT	Morphological and mechanical properties of the composite fiber	[34]	2015
PP	SWCNT	Surface characterisation and mechanical properties of composite fiber	[35]	2014
PVB	CNT	Morphology and thermal properties of developed fiber	[36]	2014
PU	MWCNT	Strain sensing behaviour of elastomeric film	[36]	2013
Epoxy	MWCNT	Mechanical properties of woven carbon fiber	[37]	2013
PP	MWCNT	Structure and electrical properties of polymer composite	[38]	2013
PVDF	MWCNT	Thermoelectric fabric	[39]	2012
Polyester	CNT	Effect of CNT on the physical properties of fiber	[40]	2011
PLA	MWCNT	Liquid sensing properties of fibers	[41]	2010
PA 6	CNT	Thermal properties of glass fibers	[42]	2009
PAN	CNT	Physical ptoperties of PAN based carbon fiber	[43]	2009
PP	MWCNT	Fiber properties with different draw ratio and comparison of functionalised CNT with pristine MWCNTs	[48]	2012

On the other hand, electro-spinning is a useful method to obtain an effective structure for biomedical application like scaffold. McCullen investigated electro-spinning of poly (L-D-lactic acid) (PLA) with the addition of MWNT for development of a scaffold for tissue engineering **[29]**. Meng reported the nano fibrous scaffold of MWNT/polyurethane composite with an average fiber diameter of 300-500 nm by electro-spinning **[30]**. They demonstrated that the composite scaffold exhibited enhancement not only to the cell adhesion and proliferation but also to the cell migration and aggregation. Hence, the nano fibrous architecture and MWNT incorporation provided favourite interactions to the cells, which implied the applicable potential of the nano fibrous composite for tissue repair and regeneration.

Melt Spun Micro-fibrillar fiber

A fibril is defined as a structural entity lying along the symmetric axis or linear dimension with specific properties of the material **[49]**. The two polymers composite often have weak interfacial adhesion, resulting in week mechanical properties of the composite. This can be upgraded to a certain extent by applying the concept of microfibrillar composites (MFCs). It was revealed that the chemical linkage between the two polymers in the case of MFC arising from trans-reaction while with the addition of condensation reactions, adhesion linkage between the two components will increase **[44-47]**. Some cases where chemical interactions between two polymers are week or not possible, a strong nucleation of microfibrils will effects on the matrix crystallization, hence to enhance the adhesion of the matrix, trans-crystallization layers can be formed. Also since the reinforcement in MFC are itself the flexible chain of polymers so along with better adhesion, advanced dispersion and improved mechanical properties are mostly expected.

Procedure to produce Micro-fibrillar fiber

Microfibrillar fibers are prepared from immiscible polymer blends, where the reinforcement is provided by fibrils of the minor component. To produce the MFC of polymer blend following requirements are necessary for the choice of polymers:

(i) polymers should have high molecular orientation so that sufficient amount of drawing has to be done to produce MFC,
(ii) melting temperature of the minor component should be more than that of the matrix polymer (approximately 230^0C) to prevent melting of fibrils during consolidation of MFC,
(iii) both polymers used should have single temperature to avoid degrading of any one of the polymer during the process,
(iv) polymers should be selected for the MFC so that the minor component forms a dispersed phase in the matrix.

The preparation of microfibrillar composites includes three basic steps:

(i) ***Mixing:*** Melt blending of immiscible polymers having different melting temperatures (Tm) followed by extrusion of these polymers;

(ii) ***Fibrillization:*** Cold drawing of the extrude of polymer blend to obtain good orientation in the different two phases;

(iii) ***Isotropisation:*** Thermal treatment of polymer blend at a temperature lying between the melting temperatures of the two polymers.

During the fibrillization of the polymer blend, polymers are converted into a highly oriented state, i.e. one of the polymer deals with an oriented blend. While during the isotropisation of the polymer blend, melting temperature of the polymer decreases and matrix transform into an isotropic matrix, as a result the polymer blend reinforced with the microfibrils of the higher melting component. Technologically, the transition of polymer blend into MFC structure take place during drawing of the polymer blend done via injection or compression molding. The essential requirement to produce the MFC structure is that the temperature at which the polymer blend processed is not close to the melting temperature of the micro-fibrils to avoid the melting of fibrils otherwise results into a spherical shape of polymer blend without fibrils.

Matrix and dispersed phase properties

Effect of viscosity ratio on micro-fibril properties

Viscosity ratio is defined as the ratio of viscosity of dispersed phase to the viscosity of the matrix. It holds one of the most influensive effect on the formation, structure and properties of micro-fibril. It is observed in different studies that the lower viscosity ratio or in other words matrix of high viscosity often yields micro-fibril of following structural characteristics:

(a) Thin micro-fibril rather approaching nano range could be formed

(b) Compared to matrix with low viscosity these fibrils have quite unsmooth surface and are shorter in length

(c) Maximum conductivity observed with high draw ratio

(d) Higher mechanical properties are also attained with lower viscosity ratio blends

Different studies have observed similar results as discussed above. Few examples of such study is being motioned below.

Examples of micro-fibrillar polymer composite

One of the study by Azadeh et al of the polymer blend polypropylene (PP) and polyaniline (PANI) to produce electrically conductive composites using PP with three different melt flow rates (MFRs) in the proportions of 80-20% is studied. Rheological behavior of the composites is studied and founds that the dynamic viscosity, as well as the storage modulus and loss modulus depends on the PP used and exhibit a different rheological behavior. It also observed that viscosity play an important role in the electrical properties of the electrically conductive composites. MFCs prepared using the polymer with the lowest viscosity shows a larger dispersed phase size in the cross-sectional. Hence, maximum conductivity of the composites observed at higher draw ratios and a more linear resistance–voltage relationship as compared to the composites prepared using the higher viscosity polymer **[4]**.

Another study of microfibrillar reinforced blends is studied using the polymers isotactic polypropylene (iPP) and polyethylene terephthalate (PET) prepared by a slit extrusion-hot and stretching-quenching process. Mechanical properties and morphology of the MFC is studied using iPP with different viscosity ratios. The morphology of the composite shows the size of dispersed phase droplet depends upon the viscosity ratio and also affects the microfibrillation of PET. Hence, for more uniform and small dispersed phase particles lower viscosity ratio is prefer. As a result finer microfibrils with narrower diameter distribution are produce at a lower viscosity ratio.

Reason behind such observations: Role of coalescence

Formation of micro-fibrils are crucially controlled by the phenomenon of coalescence. Coalescence hypothesis could be exemplified as a qualitative mechanism which involves the two droplets approaching each other and shear induction causes amalgamation of them. Through this mechanism formation of dumbbell shaped droplet followed by a three droplet dumbbell.

Here for the induction of shear; viscosity of the matrix play role. Whereby the higher viscosity matrix always induced higher shear stresses on the dispersed droplet phase forming smaller particles available for coalescence. Hence viscous matrix give formation of thin micro-fibrils with higher mechanical strength **[50]**.

Effect of compatibilizer on micro-fibril formation

Compatibilizer by nature and action act like as surfactant whose molecule is designed in such a way that one part is ‘friendly’ with one of the blend components, and another part with the other blend component. This makes it to localize the compatibilizer at the interface of matrix and dispersed phase. The main task of compatibilizer is to make an incompatible blend into compatible form by enhancing and stabilizing the two thermodynamically immiscible liquids via prevention of coalescence of droplets.

This role of compatibilizer often affect adversely on the formation of microfibrils represented in schematic **Fig. 7.** This means that for undergoing compatibilization action a coating on the spherical particles with a thin film occurs which prevents their coalescence even if in a contact. Hence it prevents the formation of microfibril.

In a research by Panamoottil *et al.* PP with PET and PP-g-MA showed mostly elliptical particles In the presence of compatibilizer, instead of smooth ‘endless’ nanofibrils. These samples were prepared to illustrate the effect of presence of compatibilizer on fibril formation, and do not contain CNTs **[50]**.

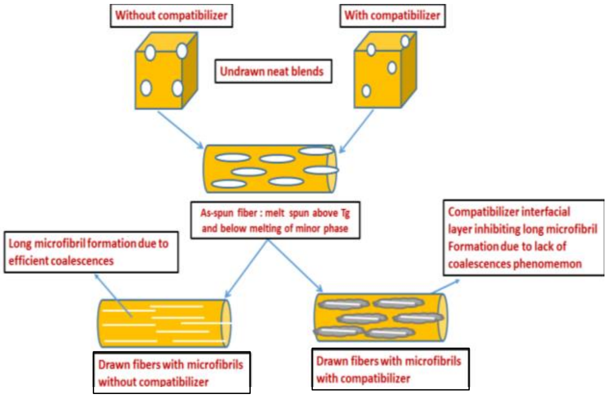

Fig. 7. Schematic showing the MFCs formation in presence and absence of compatibilizer.

Another study of polymeric matrix of PP and PET shows that with the addition of a compatibilizer and polypropylene-grafted-glycidyl methacrylate (PP-g-GMA) can increase the viscosity ratio and decrease the interfacial interaction between PET and PP which tends to decrease the size of PET phase in the unstretched form. While in the stretched form, the aspect ratio of PET microfibrils reduces in the compatibilized blends as compare to the uncompatibilized blends. Also, lower viscosity ratio results in higher mechanical properties of the microfibrillar blends. Other properties like tensile strength, flexural strength and impact toughness of the compatibilized blends are also enhanced with the addition of the compatibilizer.

So it shows still an unanswered question on the real effect of compatibilizer on micro-fibril formation. However majority of study showed smaller and lower aspect ratio of micro-fibril with compatbilizer and so this inhibiting effect of the compatibilizer on fibril formation had to be overcome when dealing with MFCs manufacturing.

To solve this problem two approaches have been carried out. The one being influenced by the study of S. Favikov *et al.* **[51]** which involved a complex process. In such a case the processing steps was followed in complex order: (i) melt blending of the polymers, (ii) extrusion of melt blend, (iii) cold drawing of polymeric matrix, (iv) pelletizing of polymeric matrix, (v) mixing of polymer blend with the compatibilizer, (vi) drying of composite, (vii) remelting of composite, (viii) re-extrusion and (ix) redrawing.

For the formation of the microfibril the compatibilizer can be loaded with filler and could be processed at a particular temperature. The research has to be focused to increase the interfacial interaction between compatibiliser and nanofiller in such a way that compatibilizer and filler lie at the interface and the functional group favor the coalescence process for formation of microfibril.

Drawing: Effect of draw ratio and drawing temperature

Structural and conductivity of MFC due to drawing

Draw ratio is an applied force or stress defined as the ratio of speed of collector roller to feeder roller. An optimum draw ratio depends on the initial dispersed phase size. For the formation of conductive fibrils and balance between the fibrils formation and breakage along the fiber axis, draw ratio plays an important role. In one of the study by Azadeh et al on PP and PAN MFC observed that with increasing the draw ratio, fibril breakages increases and conductivity decreases while the reverse is seen for lower viscosity matrix due to the high viscosity of the matrix.

Drawing temperature is another factor which influence the formation of micro-fibril. There exist two common type of drawing:

1. Cold Drawing
2. Hot Drawing

Cold drawing is the most common and favorable method after melt spinning of the fiber. In this type of drawing the temperature of the system is maintained in such a manner that the temperature of drawing is above the glass transition temperature of minor/ dispersed phase which tends to form micro-fibrils. Hence, the stretching at glass transition temperature forms the microfiber with higher aspect ratio due to the dispersed reinforcing phase to move and merge.

More overall cold drawing has been found more favorable that hot drawing in most of the studies. Martin Straat et al. founds that in polymeric blend PP/PA6 and PP/PE with carbon black (CB) and Carbon nanotubes (CNTs) on drawing in the solid state had a significant impact on the conductivity than drawing in the molten state. In the molten state, CB or CNT formed new conductive paths supported by the mobility of the matrix, while in the solid-state elongation leads to a permanent separation of filler particles from the matrix.

Effect on thermal, crystallinity and diffraction pattern due to drawing

A plastic deformation of the solid material take place during the drawing process of the material, although the drawing ratio (DR) and drawing temperature (T_D) can be diverse.

During the drawing process, the melting temperature of the material is revised hence the peak of the temperature shifts to the lower temperature with the higher drawing ratios. For the PVDF the melting temperature is 168^0C at the highest draw ratio while for the as-spun fiber its melting temperature should be 173^0C. The melting temperature of the material associates with the crystallinity of the material which could be identified by the formation of β phase, characterized through X-ray diffraction. As for the undrawn fiber, γ phase states about the melting peak of the fibre similar for the drawn fiber, melting peak can be found by increasing the T_D **[52]**.

Effect of draw ratio on conductivity was also measured by Azadeh et al in the MFC made of PP/PANI. It was observed the conductivity depends on the viscosity of the matrix as well as on the draw ratio. For the lower viscosity PP higher draw ratio is favored for better conductivity while for higher viscosity PP with lower draw ratio is having better conductivity **[48]**.

Carbon nanotubes reinforced micro-fiber: Modern model connecting traditional concept

The wave of the nanotechnology has shown the huge commercial potential in the textile industry to explore the application of nanomaterials, nanofinishing, nanocoating and nanofibre. Conventional methods used to impart different properties to fabrics do not lead to permanent effects and will lose their functions or prominent effects that impart to the fabric after washing or laundering. While with the use of nanotechnology high durability provide to the fabric due to the large surface area-to-volume ratio and high surface energy of the nano particles. Nanotechnology results in better affinity for fabrics and increases the durability of the fabric. In addition, coating or finishing of fabrics with the nanoparticles will not affect their breathability or hand feel **[57]**.

In practice, it is possible to envision polymer-polymer/CNTs bi-component fibers with a wide range of applications presently unattainable from fibers with conventional fiber spinning method. For example, the polymer/CNT composite core acts as an electrical and thermal conductor while the sheath, which can be a typical polymer, such as polyester, nylon, or acrylic, allows the dye-ability, luster, and comfort of a common textile. The energy absorbability of the bi-component fiber textile can also lead to the emergence of a new class of body armor material; while for the aromatic polymides such as Kevlar® have better energy absorbability.

Commodity textile fibers such as poly (ethylene terephthalate) (PET), polypropylene, nylon 6, nylon 66, and polyethylene are spun through the melt spinning. These fibres having a high tensile strength and modulus i.e. 0.3 GPa and 2 to 10 GPa respectively, while the elongation-to-break of the commodity textile fibres is in the range of 10 to 50%. High-performance polymeric fibers on the other hand are processed either from lyotropic liquid crystals (Kevlar® and Zylon®) or by gel spinning (Spectra®), and have strength, modulus, and elongation to break in the ranges of 3 to 6 GPa, 100 to 280 GPa, and 2 to 5%, respectively.

There is significant performance gap between the commodity textile fibers and high-performance fibres while the price of the commodity textile fibres ($40/kg) is less as compared to the high performance fibres ($5/kg). By using the carbon nanotube as filler in the polymeric materials results a good performance which matches the performance of the high-performance fibres. Hence, at low price by using CNTs, the polymeric materials have the potential to minimise the performance gap between these two classes of fibres.

There are many synthetic fillers are used for the polymeric fibre reinforcement but Carbon nanotubes (CNTs) are referred as ideal filler for the polymeric matrix. CNTs have one dimensional cylindrical geometry i.e.; nanometer-size diameter and very high aspect ratio. CNTs also show the exceptional mechanical properties while using as filler in the composites. Due to the presence of the CNTs in the polymeric matrix results in compact packing and higher orientation because of the polymer chains of CNTs vicinity (interphase) present in the composites. Polymeric matrix with CNTs strongly affects the other properties of the fibre reinforcement such as thermal stability, thermal transition temperature, fibre thermal shrinkage, chemical resistance, electrical conductivity, and thermal conductivity **[56]**. The CNTs based polymeric matrixes have great deal application related to the thermal management due to its high thermal conductivity. The CNT also shows the high breaking strengths (200 GPa) and elastic moduli (1TPa). It also possesses high value of surface area per gram approximately 500 times more and aspect ratios of around 103. These features of the CNTs spurred a great deal of interest in using CNT as filler in the reinforcing phase **[53-56]**.

Another modern approach represented in **Fig. 8** under investigation and experimentation by our group focuses on the role of modifier of modified MWCNTs on formation of microfiber. The study is mainly focussed on the effect of modification of MWCNTs through a modern modifier LiAHA ie Lithium salt of 6 amino hexanoic acid. The modifier efficiently disperse and de-agglomerates MWCNTs through electrostatic repulsion **[59]**. Further the functionalisation group of modifier reacts with matrix polymers functional group so as to interact with them and such interaction effectively effects the processing of the polymeric blends to fibers formation.

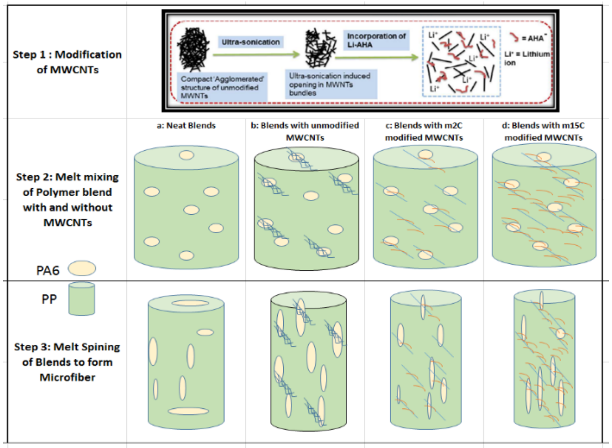

Fig. 8. Modern approach with modified MWCNTs for formation of PP/PA6 mirofiber.

Concentration effect of CNTs on fiber process ability and properties

Spinnability is demarcated by how much melt can be stretched without rupturing i.e., the maximum draw ratio

(MDR) of the material **[58]**. By increasing filler content in the polymeric material, the MDR value decreased while the modulus increased. The correlation between the elastic modulus and the spinnability is not clearly related, but it certainly exists and it is theoretical say that elastic modulus indicates the rough spinnability.

In another study by Sertan Yesil *et al.* **[60]** on HDPE/PET with CNTs; it was observed that with adding the small amount of CNT in the polymeric composites in the PET phase, the surface structure of the microfibers changes. The surface structure of the microfibers also depends on the concentration of the CNT in the composites **[61]**. The concentration of the CNT in the composite also effects the fibrillation of the PET phase. As the CNTs are rigid particles, limits the flow of the polymer melt hence increase the melt viscosity of the polymer. With decreasing the amount of the CNT in the PET phase, hot stretching of the polymer facilitate the deformation as a result fibrillation of the dispersed PET/CNT phase in the composite take place. This is more effective due to the lower melt viscosity of dispersed phase. Hence with increasing the PET content in the composites and decreasing the CNT content in PET phase, the concentration of the microfibers raises up and the average diameter of composites decreases.

Functionalization on CNT effecting fiber process ability and properties

In order to develop the outstanding mechanical properties of the composites, the adequate interaction between the polymer matrix and the CNT should take place. Also for the better results and higher orientation modification of CNT is preferred. To prepare the microfiber of polymer blend with CNT, the alignment of CNT in the matrix should take place by spinning technique which increases the mechanical as well as physical properties of the CNT/polymer composites. The CNT can orient only in the x- or y-direction so it scarcely facilitated as isotropic materials. Also CNT filled polymer composite, increases the strength of the composite while the modulus can sacrifice of toughness and ductility, due to embrittlement **[62]**.

In a study by Zhong-Ming Li *et al.* CNTs has been functionalised with –COOH and solution blended with EVA to cause an interfacial bonding between the two. Further this filler mixture is added for MFC formation in matrix polyethylene and dispersed phase of polycarbonate. It was found that MWCNTs with –COOH groups predominantly localize in the PC micro-fibrils without evident migration, which implies the strong interfacial bonding between CNTs and EVA copolymer by increasing the anchoring (or interacting) sites along the nanotubes with EVA copolymer **[63]**. Using the SEM, it is clear that most nanotubes were embedded and tightly held to the matrix which is the indication of the strong interfacial bonding between the CNTs and EVA. Hence, it is capable of transferring the stress load though out the matrix and preventing the sliding of nanotubes during tension. On the other hand, the interfacial adhesion between the CNT/PC microfibrils and PE matrix also shows good results, which is observed by comparing the results of pure PC/ PE matrix with EVA and without EVA for MFC formation.

Another work on polymer blend HDPE/ PET with CNTs shows improved mechanical properties by increasing the tensile strength and modulus of the matrix with the presence of CNTs in the matrix. For the better mechanical properties such as tensile strength, CNTs are modified to generate hydroxyl and carboxyl group on the surface the CNT referred as pCNT and mCNT. Due to the week interfacial adhesion between PET and CNT, it is observed that the PET/CNT composite shows weak mechanical properties due to the week sites of CNTs, which causes the pull out of CNT from the surrounding matrix during the spinning process. With the modification of the CNTs, carboxyl and hydroxyl groups formed on the CNT surface can react with the carboxyl end groups of PET which increases the chemical compatibility in the composite. Moreover, these carboxyl and hydroxyl sites on the CNT surface can increase the mechanical interlocking and covalent bonding between CNT/PET matrixes. Modification of CNT with polyethylenglycol (PEG) also shows different modes of reaction patterns with PET due to the hydroxyl end groups of PEG can interact with the carboxyl end groups and aromatic group of PET which enhanced the results. Hence, the interactions between the PET and CNT with the modification of CNT improve the efficiency of load transfer from the PET to CNT results in better mechanical properties of the composites. Later, it is clear that the matrix prepared with pCNT and mCNT shows better result as compared to the PET/CNT composite without modification due to the presence of defect sites on the CNT surface **[64]**.

Conclusions and future outlook

Micro-fibrillar composite have its great importance in terms of enhancement of dispersion of reinforcing filler and providing qualitatively better adhesion between the matrix and reinforcing particles. This definitely leads to enhancement of mechanical strength along with increase in conductivity. In addition to these basic advantages of the micro-fibrillar composite the advanced importance of it lie by removing the second blend component and collecting the fibrils out of it and finding its utilization. It is supposed and also observed that by removing the second (minor) component out of the major one, micro to nano porous structure could be formed with very high specific surface area which marks them reasonably attractive for biomedical applications such as regenerative medicine as well as carriers for controlled drug delivery.

Future of MFCs is wide open both in the area of mechanical composites and for biomedical applications. It is needed to have more research oriented towards applications. For better composites nanofillers with different modifiers and combatibilizers should be tried and optimized conditions should be generalized for definite properties. With respect to biomedical applications of MFC it's quite still at infantry stage and so has wide scope of success in this field. Matrix and dispersed phase polymers of biocompatible nature should be blended with biocompatible nanofillers and their properties should be well analyzed for broadening the area of MFCs and for better utilizing this traditional concept for accomplishment of the modern approach.

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