THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 4 - 2018, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2018.4.03

POLYMERIC BLENDS: A SHORT REVIEW

Mihaela Claudia GOROVEI, Marina BUNEA, Adrian CÎRCIUMARU, Iulian Gabriel BÎRSAN
“Dunarea de Jos” University of Galati, Romania
e-mail: adrian.circiumaru@ugal.ro

ABSTRACT

At present, the use of polymeric materials is so intense in our society, that we could consider ourselves to be living in the „polymer age”. Due to their versatility, polymers are present in every step of our whole „infrastructure”. It is a growing research field due to the need of extending the application horizon of polymers with the purpose of replacing other materials (e.g. metallic) that are predominantly used in certain industries. This article is a review that discusses both the classification of polymer materials and state-of-the-art research of other authors with respect to polymer blends.

KEYWORDS: polymeric blends, nanoparticles, synthesis, classification

1. Introduction

It is known that the materials composed of polymers have been part of our civilization since prehistoric times. Polymers are abundant in nature, found in all living systems and materials such as wood, paper, leather, natural fibers, which are used extensively. While natural polymers retain their intrinsic importance, nowadays the synthetic materials are mostly used [1–4].

The term "polymer" is derived from the Greek words *poly* ("many") and *meros* ("part"). Quite literally, a polymer consists of "many units". Polymers are formed from a large number of identical small molecules, called monomers [5].

There are six main areas of polymer application: plastics, rubbers or elastomers, fibers, surface finishes, floor protection by coatings, and adhesives (Fig. 1) [6–9].

Polymers are macromolecules constructed by linking together a large number of much smaller molecules resulting from the chaining of a large number of small monomer molecules linked by covalent bonds. Polymers are obtained from polymerization reactions [10-15].

Fig. 1. *Examples of polymer applications* [16]

Polymer technology is considered a mature technology and relatively easy to achieve through complex forms of most materials in a cost-effective mean. Since most polymers are low-density materials, they have specific service advantages in transport and metal replacement, thus becoming important. Polymeric materials dominate packaging applications and environmental pressures will ensure that recycling and reuse of this type of waste will continue to be an important development area [8, 17, 18]. Also, a number of new applications are emerging as a result of major advances in the domain of molecular and cellular biology.

Polymers were initially classified by Carothers (1929) in condensation and addition polymers based on the compositional difference between the polymers and the monomers from which they were synthesized [10, 19-21].

2. Polymer classification

Polymers can be classified according to several criteria (Table 1). The most obvious classification is based on the origin of polymer, i.e., natural or synthetic. Of course, polymer classifications can be more elaborate, from polymer structures, mechanisms of polymerization, preparation methods, up to thermal behaviour, monomer chemical nature, growth mechanisms of polymer chains, among more others.

Table 1. *Types of polymers* [20, 22-28]

Nomenclature	
BIS-GMA - bisphenol A glycidyl methacrylate	PET - polyethylene terephthalate
C – carbon	PGA - poly (glycolic acid)
CF – carbon fibres	PHB - polyhydroxybutirate
GF – glass fibers	PHEMA - poly (HEMA) or poly (2-hydroxyethyl)
HA - hydroxyapatite / hydroxylapatite methacrylate	PLA - poly (lactic acid)
HDPE - high density polyethylene	PLDLA - poly (L-DL-lactic acid)
KF – Kevlar fiber	PLLA - poli (acid L-lactic)
LCP - liquid crystal polymers	PMA - polymethylacrylate
LDPE - low density polyethylene	PMMA - polymethylmethacrylate
MMA - methyl methacrylate	POLIGLACTIN - PLA and PGA copolymer
PA – polyamide	POM - polyoxymethylene - polyacetal
PBT - polybutylene terephthalate	PP - polypropylene
PC - polycarbonate	PS - polysulfone
PCL - polycaprolactone	PTFE - polytetrafluoroethylene
PE - polyethylene	PU - polyurethane
PEA - polyethylacrylate	PVC - polyvinyl chloride
PEEK – polyetheretherketone	SR - silicone rubber
PEG - polyethylene glycol	THFM - tetrahydrofurfuryl methacrylate

Polymers can be either natural or synthetic. All the conversion processes that occur in our body (e.g. energy generation from food intake) is due to the presence of enzymes. Polymers of biological origins are enzymes, proteins and nucleic acids, as well. There are a large number of synthetic (artificial) polymers that are composed of different groups: fibers, elastomers, plastics, adhesives, etc. Each group itself has subgroups [29-31].

2.1. Classification based on polymer structure

Linear, Branched or Reticular, Ladder vs. Functionality:

Linear Structure

If a polymer is made of highly difunctional monomers, the result is a linear polymer chain.

The term linear may be somewhat misleading, however, because molecules do not necessarily require a linear geometric conformation as shown in Figure 2(a).

Branched structure

If several molecular reactions with three (or higher) functionalities (either intentionally or by side reactions) are introduced, the resulting polymer will have a branched structure.

One such example is the grafting of the branches made from the repeating unit "B" to a linear backbone of the repeating units. Here it is said that B is grafted on A (Figure 2(b)).

Reticular structure

As the length and frequency of branches on polymer chains increases, the probability that the branches eventually reach from one backbone chain to another increases. When backbone is connected in this way, the molecular structure becomes a network, with all chains linked by covalent bonds (Figure 2(c)) [7, 19, 32].

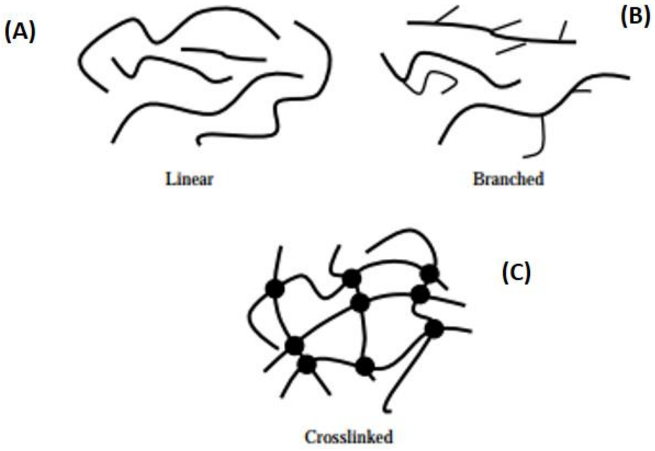

Fig. 2. *Schematic representation of polymer structures* [6]

Amorphous or crystalline state

Depending on structural state, the solid-state polymers can be considered amorphous, crystalline or, in some cases, semi-crystalline. In the cooling step of the molten-state polymer, molecules usually are attracted together leading to a relatively strong aggregation which forms a solid of low potential energy.

Homo/Co-polymers

When discussing composition, polymers can be copolymers or homopolymers. Polymers composed of a single repeat unit in the polymer molecule are known as homopolymers. In any case, chemistry researchers have developed techniques to build polymer chains that contain more than one repeated unit. Polymers composed of two different repeating units in the polymer molecule are defined as copolymers [7, 19].

Polymer classification based on the degree of stereoisomerism relative to the configurations of units in a chain:

- Geometrical isomerism - is understood as different configurations of substituents on a carbon-carbon double bond or a cyclic structure.
- Optical isomerism - comes from different configurations of substituents on a saturated carbon atom.

Classification of polymers based on the results of the polymer chain growth mechanism:

- Stable growth polymers (polycondensation)
- Chain polymerization (e.g., free radicals, anionic and cationic radicals).

3. Polymerization

Polymerization by chain or addition: Polymer chains increase by repeated addition of monomer molecules to an active chain centre, contrary to stepping polymerization. The polymerized chain can be made by free radicals and ionic moieties [33, 34].

Radical free polymerization: In free radical polymerization, three basic reactions occur during polymerization. These are initiation, propagation and termination reactions. In the initiation reactions there is continuous generation of free radicals.

Ionic polymerization: Ionic polymerization is a chain process that is used on an industrial scale to produce thermoplastic polymeric materials.

Anionic polymerization: Anionic polymerizations are industrially used for the production of thermoplastics, especially formaldehyde and e-caprolactam and block copolymers (e.g., styrene-butadiene-styrene type thermoplastic elastomers) [35-37].

Cationic polymerization: Cationic polymerization is defined as a polymerization reaction of adhesion mediated by a propagating carbocyte.

Stage growth or condensation polymerization: Forms the lifespan of the growing polymer chain until the functional group reaches its end [38].

4. Nanoparticles and their role in polymer composites

Nanoparticles (NP) are a wide class of materials that include substances in the form of particles that are at least one size less than 100 nm. Depending on the global form, these materials can be 0D, 1D, 2D or 3D.

For the preparation of nanoparticles, most methods are performed in the emulsified system, involving two steps: preparing an emulsified system and forming nanoparticles by precipitating/gelling a polymer or polymerizing the monomers. Other methods of nanoparticle manufacturing are possible that do not involve their preparation from an emulsion, one example is the microfabrication process that produces nanoparticles from solid templates. In addition, nanoparticles can be manufactured by an inter/intramolecular crosslinking process. However, emulsification pathways and polymerization emulsion remain the most commonly used methods of preparing polymeric nanoparticles. [39-63].

5. Short review regarding synthesis of polymer blends

Aziz Babapoor and his collaborators have manufactured and characterized the nanoparticle-nanoparticle composites with electrophoretic/electrospinning phase change materials. The following conclusions can be drawn from the experimental results:

(a) The diameter of the fiber is strongly dependent on the electrical conductivity of solutions; for example, the fiber diameter is reduced to a higher electrical conductivity value. The smallest average fiber diameter of 59 nm for Fe^{-4} was found;

(b) FTIR results indicate that the addition of Al_2O_3 nanoparticles has a significant impact on PEG crystallization structure, and there is a strong interaction between Al_2O_3 and PEG;

(c) Of all the tested composites, the initial SiO_2 composite temperature was the highest, while the Al^{-2} composition provided the maximum temperature [64].

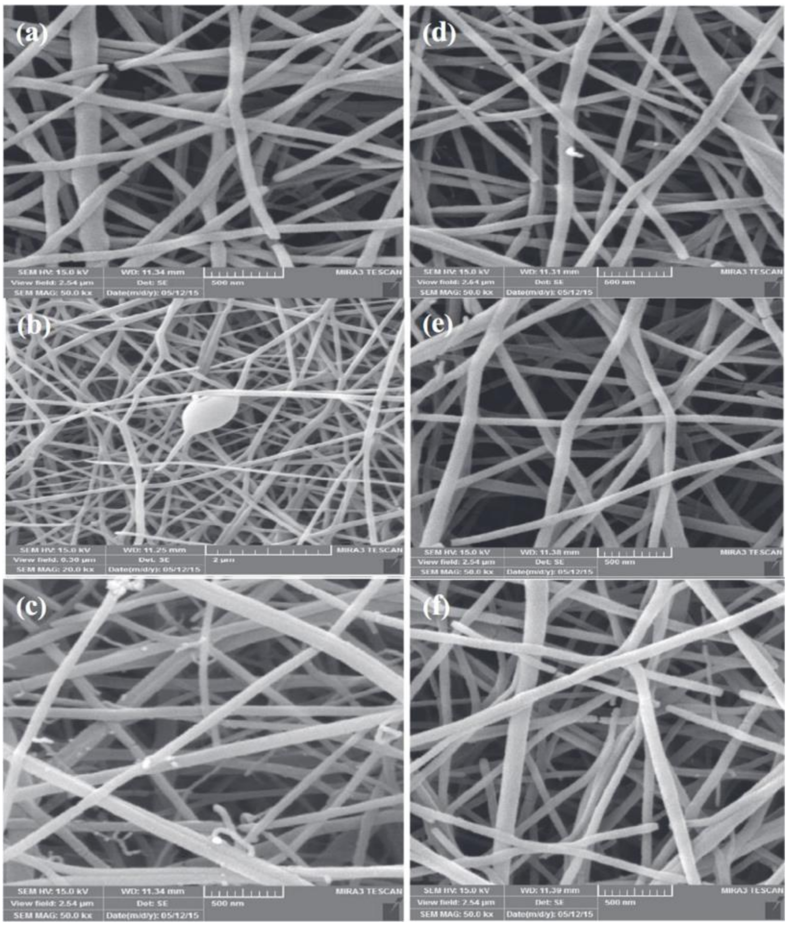

Fig. 3. *SEM images of nanofibers (a) Al^{-2}, (b) Zn^{-4}, (C) Si^{-2} and (d) Fe^{-1}* [64]

S. E. Jasim and his collaborators have manufactured superconducting nanoparticles YBCO (Yttrium, Barium, Copper Oxide) by electrochemical electrospinning method. The sample was prepared by dissolving 4 g of Y-Ba-Cu acetate and 3 g of PVP powder in 25 mL of a mixture of propionic acid, acetic acid and methanol [65].

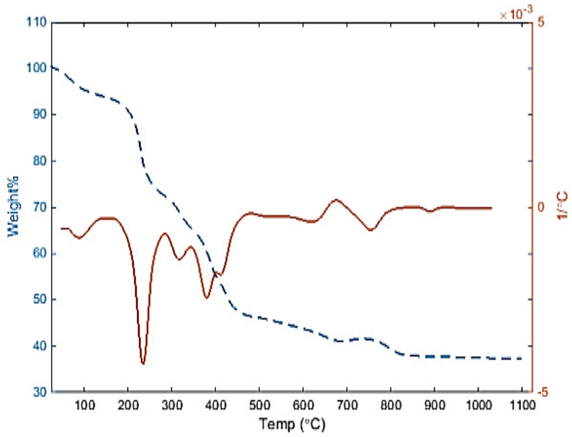

Fig. 4. *Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) of YBCO electroplated nanoparticle samples* [65]

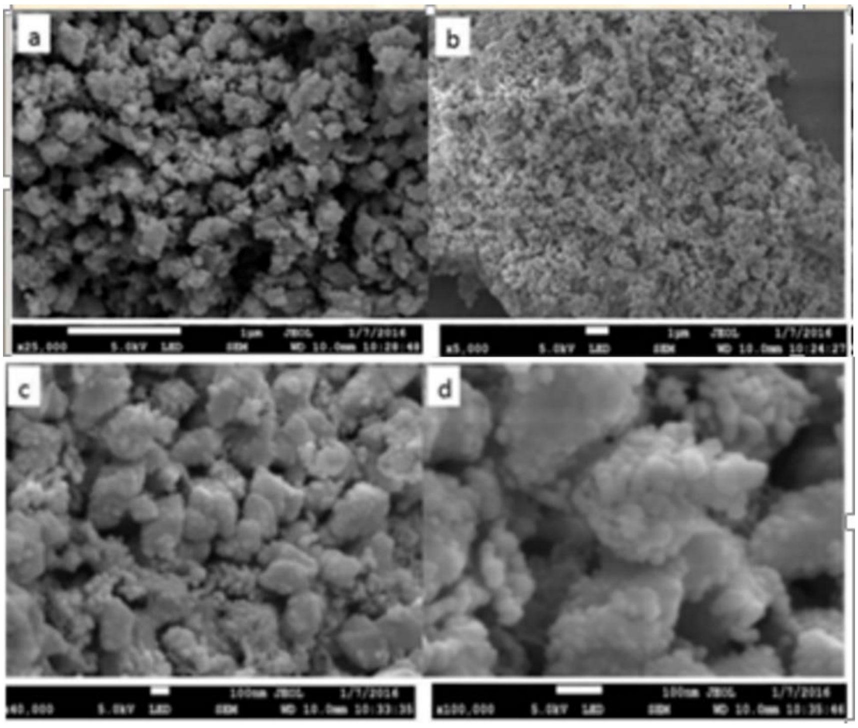

Fig. 5. *FESEM images of YBCO HTS nanoparticles (a), (b) after first heat treatment and (c), (d) after second heat treatment* [65]

The YBCO nanoparticle thin film temperature transition showed a zero resistance at 78 K with a semi-sharpened transverse width of 13 K. While the blank samples showed zero resistance at 85 K and a sharp transition width of 6 K. A typical nanoparticle diameter between 20 and 50 nm was obtained and agglomerated nanoparticles of about 388 nm were obtained. The measured area of the YBCO nanoparticle was higher than that for the semi-finished product and was not influenced by the calcination temperature [65].

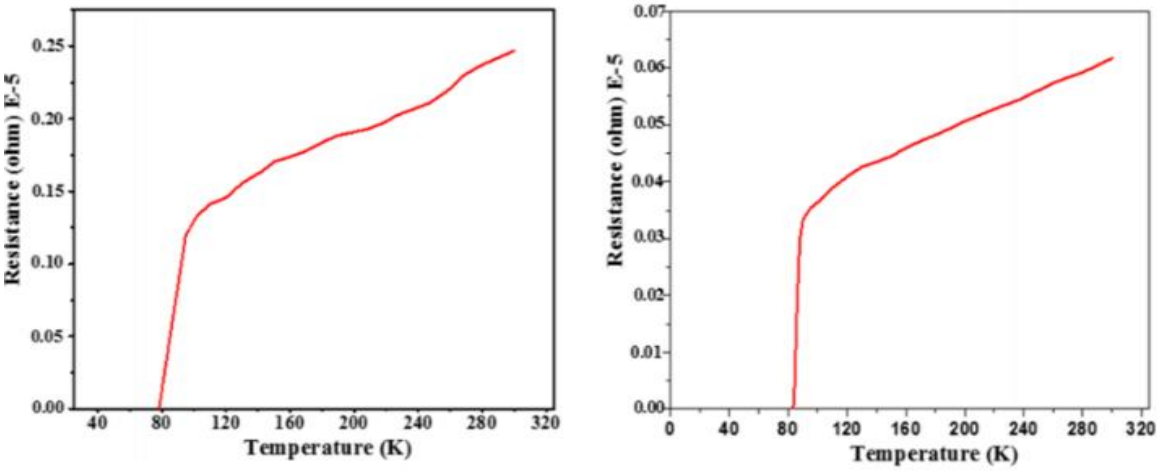

Fig. 6. *Tc measurements of YBCO HTS, (a) thin film nanoparticles Tc = 78K, (b) block sample Tc = 85K* [65]

Yun Wei *et al.* have manufactured TiN/carbon nanotubes by the electrospinning method. They synthesized TiN / carbon nanofibers by electrospinning of a polyvinylpyrrolidone (PVP, Mw = 1,300,000) and tetrabutyl titanate ($Ti(OC_4H_9)_4$), followed by two-stage heat treatment processes for nitration. $Ti(OC_4H_9)_4$ was dissolved in 10 mL ethanol (PVP was added to the mixture to control the viscosity of the solution).

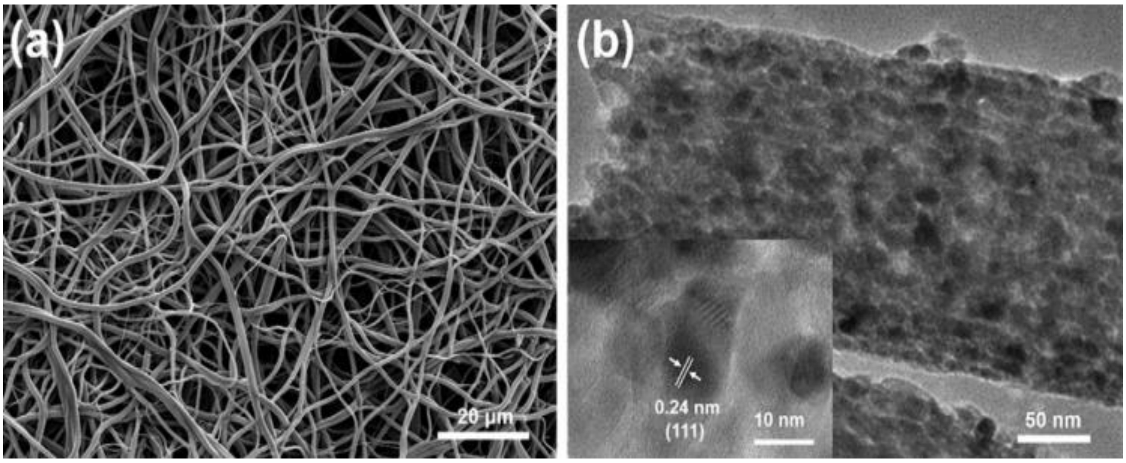

Fig. 7. *SEM (a) and TEM (b) images of TiN/carbon nanofibers under the insertion* [66]

Ti-containing polymer nanofibers were collected on the substrate by application of a high voltage of 11 kV. Polymeric nanofibers were calcined at 280 °C in air for 2 hours to obtain precursor nanofibers. Next, the synthesized precursor nanofibers were calcined in an oven under an ammonia atmosphere at 900 °C for 4 hours.

Finally, after the sample was cooled to room temperature under ammonia, the TiN/carbon counterparts were obtained.

The nanofiber morphology was examined with an electronic scanning microscope and an electronic TEM transmission microscope, at a 200 kV accelerating voltage [66].

Lu *et al.* have prepared PVP/Ag_2S nanoparticles in ethanol solution by Qian's method.

In a typical procedure:

- 0.1 g of $AgNO_3$ was dissolved in 3.45 g of ethanol with vigorous stirring, then various amounts of PVP (0.15, 0.31 and 0.48 g) were added and stirred for about 10 minutes to obtain different concentrations of PVP (4, 8 and 12 %v/v).
- an excess amount of CS2 was then introduced into the three solutions and stirred in the absence of light to allow sulfurization reaction for 24 hours to obtain different PVP/Ag_2S ratios (5.2:1 for 4%PVP, 10.6:1 for 8% PVP and 16.6:1 for 12% PVP).

The black viscous solution obtained was loaded into a plastic syringe equipped with a 14 cm platinum needle. The needle was connected to a high voltage source (15 kV) which was applied to the electro-spin.

A piece of flat aluminum foil was placed 20 cm from the tip of the needle to collect the nanofibers. Electrospinning was performed in air.

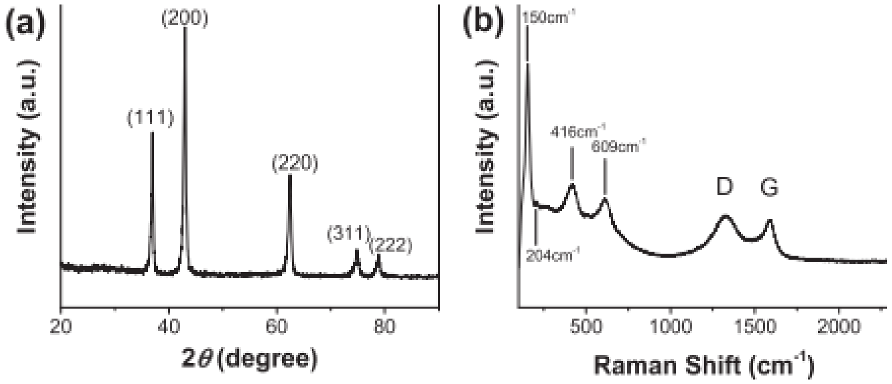

Fig. 8. *XRD (a) and Raman (b) spectra of prepared TiN/carbon fibers* [66]

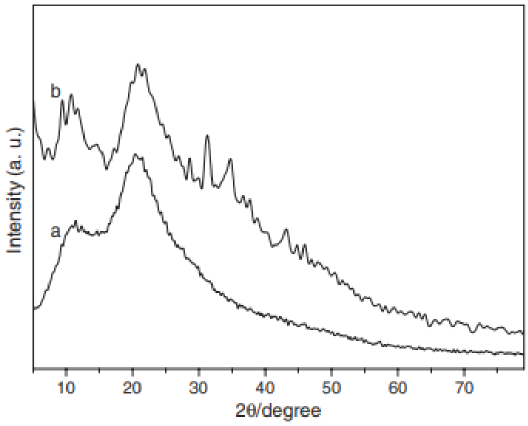

Fig. 9. *XRD patterns of (a) PVP and (b) PVP/Ag2S electro-spin composite fiber film* [67]

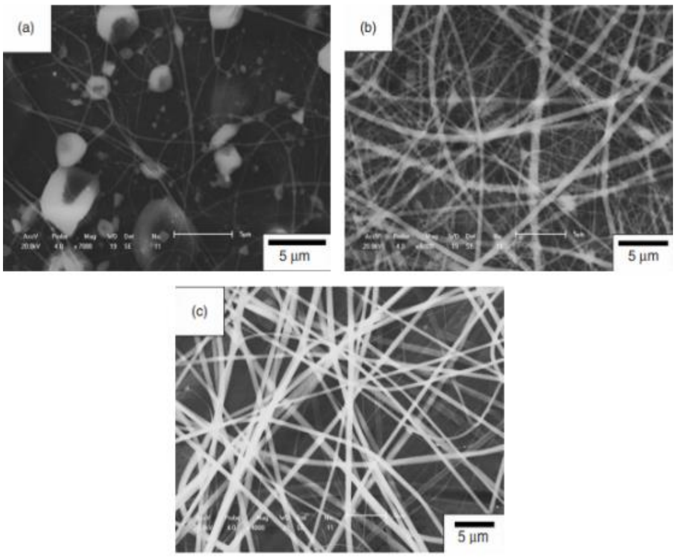

Fig. 10. *SEM images of PVP/Ag_2S composite fibers with different PVP concentrations. (a) [PVP] = 4% by mass; (b) [PVP] = 8% by mass; (c) [PVP] = 12% by mass* [67]

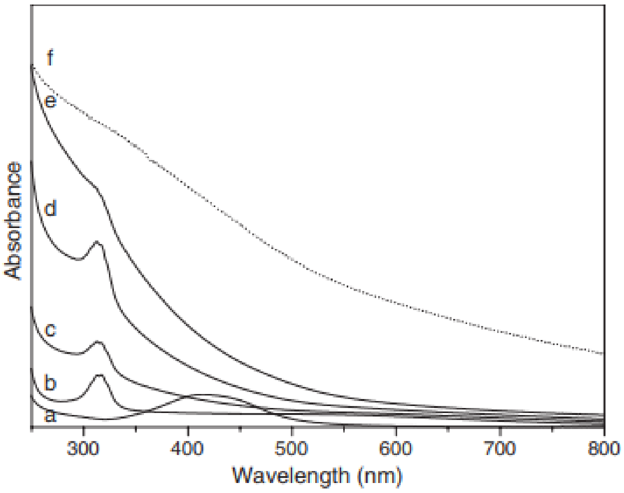

Fig. 11. *UV-vis spectra of PVP-$AgNO_3$ ethanol solutions with or without CS_2 at different reaction times and electro-spin PVP / Ag_2S composite fiber film: (a) PVP-$AgNO_3$ ethanol solution after agitation for 10 minutes; (b) - (e)) PVP / Ag_2S ethanol solution with a reaction time of 5 minutes, 2 hours, 6 hours and 24 hours; (f) PVP / Ag_2S glass fiber electroplating* [67]

Figure 12 shows TEM images of PVP/Ag_2S fibers which were electro-spinned from a solution containing 8% by weight PVP [67].

Vyacheslav V. *et al.* fabricated composite fibers by the intermediate electrospinning method containing $ZrOCl_2$ and $Al(NO_3)_3$ as ZrO_2 and Al_2O_3 precursors with PVP as additive. Figure 14 (A) discloses the microstructure of $ZrOCI_2$/$Al(NO_3)_3$/PVP for the manufacture of fibers. The average filament diameter is 284±69 nm. Data obtained by EDS indicate that the fibers prepared as an electrospinning solution contain the precursors of the polymer, ZrO_2 and Al_2O_3 (Zr, Cl, Al, N) [68].

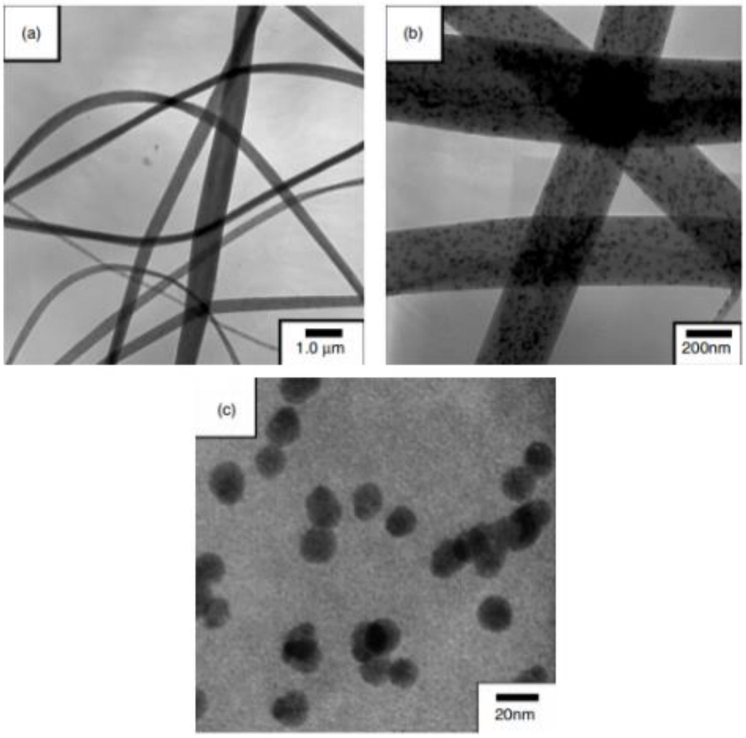

Fig. 12. *TEM images of PVP/Ag_2S composite fiber: [PVP] = 8% by mass* [67]

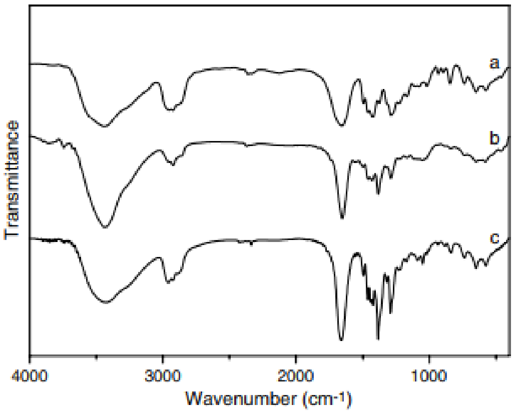

Fig. 13. *FTIR spectrum of (a) PVP, (b) PVP/silver nitrate fibers, (c) PVP/Ag_2S fibers* [67]

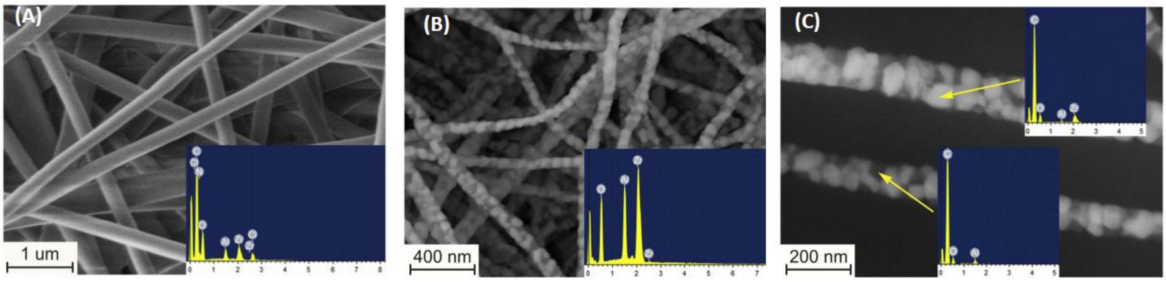

Fig. 14. *(A) SEM image of $ZrOCl_2$/$Al(NO_3)_3$/PVP fibers before calcination. The insert presents the EDS spectrum; (B) SEM image of $ZrOCl_2$/$Al(NO_3)_3$/PVP fibers is calcined at 1200 °C. The EDS spectrum is inserted; (C) SEM image of individual ceramic nanofibers. The inserts present the results of the local EDS analysis* [68]

The presence of the two distinct phases can be clearly seen in Fig. 14(C): ZrO_2 (brighter phase) and Al_2O_3 (dark phase). It should be noted that Al_2O_3 is partially dissolved in ZrO_2 (upper insert in Fig. 14(C). The carbon peak comes from the conductive tape used to fix samples for SEM visualization.

The formation and evolution of the crystalline structure of the composite fibers with the increase of calcination temperature is shown in Fig. 15. It can be seen that the $ZrOCl_2$/$Al(NO_3)_3$/PVP fibers before the thermal treatment are amorphous. The complete decomposition of the bonded polymer, zirconium and aluminum salts at 500 °C has no effect on the main crystal reflections at $2θ$ = 30.2°, 35.2°, 50.2° and 60.2° [68].

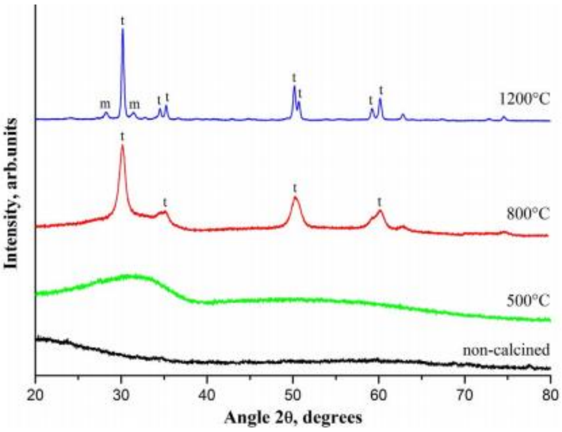

Fig. 15. *XRD formats of calcined $ZrOCl_2$/$Al(NO_3)_3$/PVP fibers at different temperatures; m - the monoclinic phase of ZrO_2, t - the tetragonal phase of ZrO_2* [68]

Guo-Xun Sun *et al.* have manufactured zirconium nanofibers. Zirconium carbonate ($CH_2O_7Zr_2$), acetic acid (CH_3COOH), Nitrogen nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$) were added to the experiment. Under stirring at 30 °C-40 °C, the appropriate amount of PVP (molar ratio Zr (atoms): PVP = 1:0.001-0.0012) mixture is added to the solution.

Gel fibers were obtained using electrospinning method. The effect of the process parameters (voltage, collection distance and flow) on fiber morphology and diameters have been studied. The processes were synthesized under the following electrospinning conditions: the voltage was in the range 18-20 kV, the collection distance in the range of 10-12 cm and the flow rate in the range of 0.7-1.0 mL/h.

Zirconium nanofibres were obtained after sintering at 1200 °C (holding time, 2 hours) under an air atmosphere. The gel fibers were sintered from room temperature to 300 °C with a temperature rise rate of 0.5 °C/min, 1 °C/min from 300 °C to 800 °C, with time-keeping time one hour and 5 °C/min from 800 °C to 1200 °C.

SEM image (Figure 16(a)) indicates that the fibers have diameters of 400-600 nm. The fibers showed moderate flexibility. Observation of a single fiber (Figure 16(b) and (c)) indicates that the fiber is made from 20-40 nm granules and does not contain cracks, having a smooth surface. The SEM image from Figure 16(d) has a dense and smooth cross-section of the fiber.

Figure 16. shows the XPS survey spectrum and the high resolution of the detailed spectra of calcined ZrO_2 fibers at 1200 °C, the sample contains only Zr, Y, O, and a small amount of carbon. The existence of the C 1s peak is mainly caused by CO_2, which is absorbed by the surface of the sample. The XPS spectrum of the sample exhibits peak Zr $3d_{5/2}$ peak energy of 181.4 eV, Y $3d_{5/2}$ peak of 156.7 eV [69].

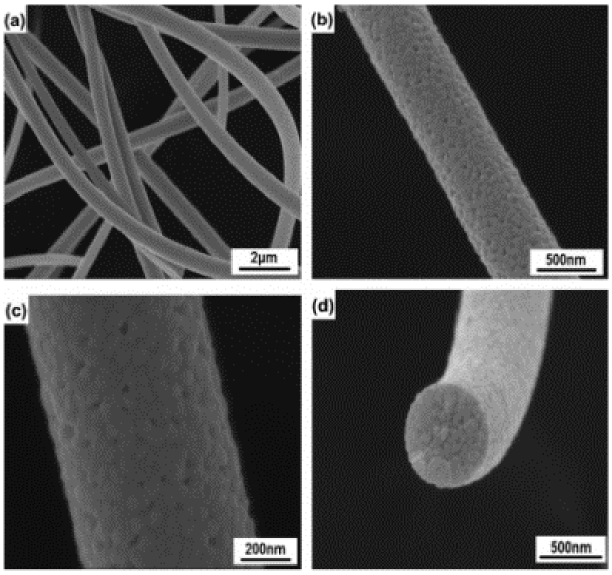

Fig. 16. *SEM images of fibers after calcination at 1200 °C* [69]

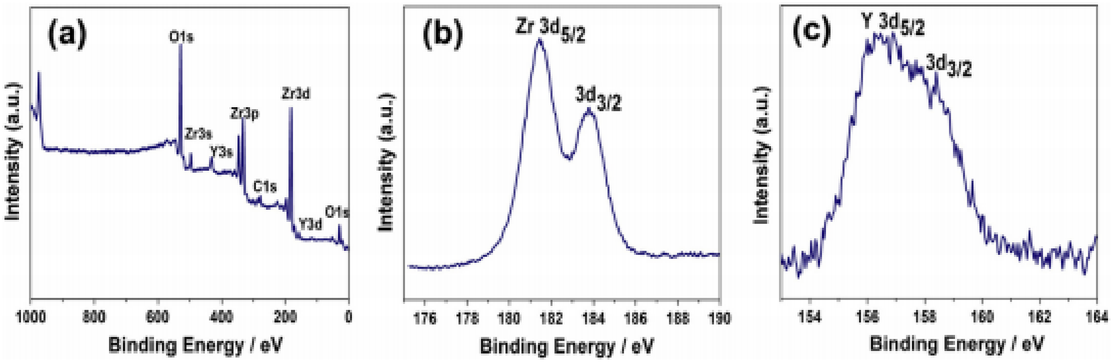

Fig. 17. *XPS spectra of (a) survey scan, (b) Zr 3d double, and (c) doublet of 3D in ZrO2 fibers calcined at 1200 °C* [69]

The absorption maximum at 1628 cm^{-1} is attributed to the bending vibration of H_2O. Absorption peaks (1556, 1456, 1352, 1032, 954 and 647 cm^{-1}) are attributed to bending vibrations of CH_3COOH functional groups, which can prove CH_3COO and Zr^{4+} binding. The broad absorption velocity at 470 cm^{-1} is the common contribution of the polymer in the Zr-O-Zr chain. From the data above, the minimalist structural formula of the zirconium acetate can be speculated as $ZrO(OH)(CH_3COO)\cdot H_2O$.

The process of idealized spinned soil in the experiment is shown in Figure 17. The transition in the soil solution is the first stage. At this stage, the possible structure of the poly-zirconia acetate (PZA) and the idealized formation of the PZA were speculated. In the second step, polyvinylpyrrolidone (PVP) was added and mixed with soil particles. Then, during the spinning process, there was a transition of sol-gel (gelation). The soil particles were dried, crosslinked and finally assembled into the gel with a coherent mesh.

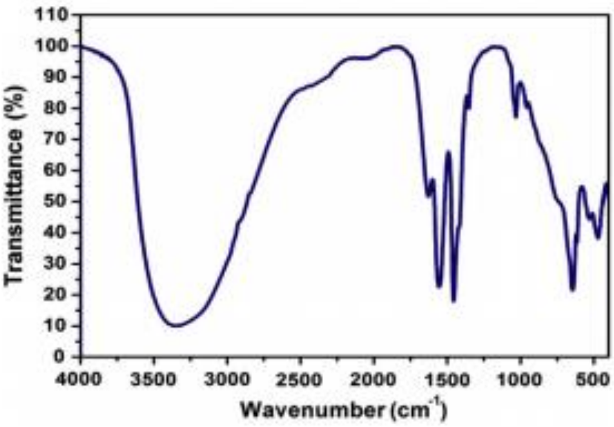

Fig. 18. *Infrared Fourier Transform Spectroscopy (FT-IR) of PZA* [69]

From the TG-DTA curves of the gel fibers, which is shown in Figure 19 it can be seen that the fibers have undergone three weight loss stages from room temperature to 800 °C, with a total loss of approx. 48.3%. The 24% weight loss below 240 °C was due to the loss of solvents including water and acetic acid.

From 240 to 450 °C, weight loss was approximately 19% corresponding to the decomposition and carbonization of PVP and acetic acid, which accompany the removal of solvent molecules in the gel network.

The weight loss of 5% between 450 °C and 700 °C corresponds to the expulsion of water molecules formed by the dehydroxylation of the materials together with the removal of the residual carbon by oxidation.

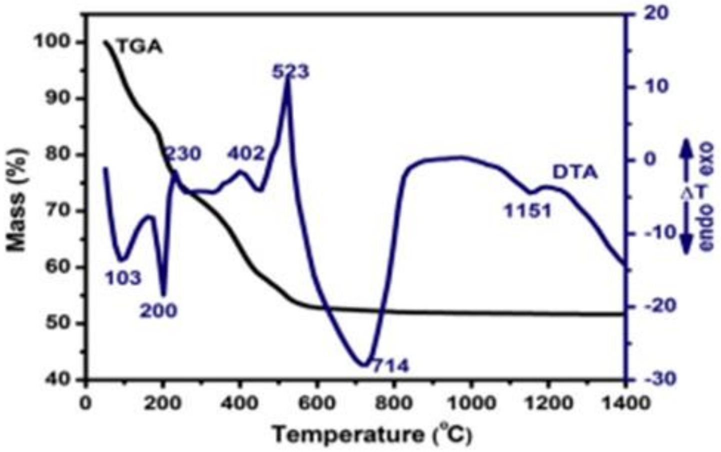

Fig. 19. *TG-DTA curves of gel fibers* [69]

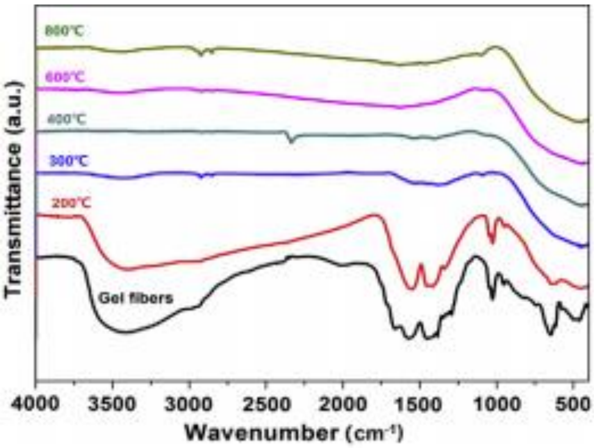

Fig. 20. *FT-IR spectra of gel fibers and calcined fibers at different temperatures* [47]

In the DTA curve, the rise of endothermic peaks at 103 °C and 200 °C may be due to the removal of adsorbent water, bound water and some organics in gel fibers.

Both weak, the exothermic foot at 230 °C and the exothermic peak at 402 °C corresponded to the decomposition and carbonization of acetates and PVP.

The carbon combustion and initiation of crystallization was indicated by the exothermic peak at 523 °C, which was confirmed by XRD results.

The endothermic peak at 714 °C was attributed to the growth of ZrO_2 granules. The low endothermic peak at 1151 °C was mainly attributed to the further increase of ZrO_2 grains [47].

5. Conclusions

Internal properties of materials such as solubility, interactions between polymer and payload, polymer chain flexibility, surface loading, stereochemistry, surface chemistry, molecular weight and crystallization capability, etc. should be taken into account in choosing the right method of preparation and appropriate processing.

Design of polymer blends is an interesting alternative for obtaining micro and nanostructured surfaces.

The cost is reasonable and does not contain time-consuming procedures.

Despite the crucial role of superhydrophylic and superhydrophobic surfaces play in the final application of the material, so far, most studies on polymer blends have been linked to control of physical and chemical properties, their barrier properties or electrical conductivity.

From the current review, it appears that control of polymer nanostructure and addition of nanoparticles has led to improvements in structural and functional properties in a number of polymer systems as a response to continuous requirements in advanced industrial sectors.

The availability of new nanoparticles with extraordinary properties (i.e. carbon nanotubes, graphites, but also nanoclays, nanocellulose, metals and ceramics) leads to new and interesting possibilities for a continued expansion of the polymer markets.

Acknowledgements

This work has been funded by the European Social Fund through the Sectoral Operational Programme Human Capital 2014-2020, through the Financial Agreement with the title „Burse pentru educaţia antreprenorială în rândul doctoranzilor şi cercetătorilor postdoctorat (Be Antreprenor!)", Contract no. 51680/09.07.2019 - SMIS code: 124539.

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