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Review of polyacrylonitrile blends and application in manufacturing technology: recycling and environmental impact



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Keywords: Blend Polyacrylonitrile Polymers Properties Recycling	The blending of polymers provides a method of obtaining materials with improved property from the parent compounds. This review focused on polyacrylonitrile (PAN) blends, its applications, the recycling possibility of PAN and its environmental impact. The review is also intended to shed insight into rPAN materials recycling possibility for domestic, industrial and manufacturing applications. It will also assist in the understanding and production of PAN and rPAN based products.

1. Introduction

In the field of polyacrylonitrile (PAN) development, research into the improvement and application are still ongoing with regards to the technological development of different blends. These blends are now having versatile application in domestic, industrial and major manufacturing processes. The improved PAN technological advancement is paving ways to different viable methods of improving the compatibility and production processes of its products in the desired applications [1–4]. The acrylonitrile is employed as a co-monomer with styrenes such as Acrylonitrile Butane Styrene (ABS), Acrylonitrile Styrene Acrylate (ASA), and Styrene Acrylonitrile (SAN) as shown in Fig. 2. These PAN products have many industrial, transportation and manufacturing applications. Therefore, further exploration, development and recycling of both the neat and used polyacrylonitrile are needed. These can be achieved by blending PAN with other polymers, because of its versatile applications.

Thus, researchers are looking for ways of improving its production through blending. Polymer blending is the material properties combination processes such as chemical, thermal and mechanical properties of different polymers to form improved products as desired by the market factor. The blending processes are now versatile due to the advancement in different technological development with improving processability in state of art facilities, especially in the manufacturing of items with smart applications [5–9]. However, the blended properties of some PAN material are often not sufficient in their application, therefore the addition of fillers such as nanoparticles are required [10]. These fillers assist and influence the processability by changing the rheological properties of PAN and its blends. This changing effect needs exploring further for effective material development. In addition, fillers of nanoparticles in scale efficiently influence the electrical, chemical and mechanical properties of polymer materials when compared with microparticles of other material of the same volume fraction. Therefore, nano-particle particles are gaining scientific interest in the development of PAN and rPAN products [5,11–16].

This review focused on the need for the technological improvement of PAN products, recycling of PAN waste and its environmental impact.

2. Polyacrylonitrile (PAN)

PAN under the trademark of Orlon was prepared and marketed by DuPont as-spun fiber in 1941. PAN a highly versatile polymer due to its high carbon content. Its carbon-carbon backbone guarantees high biostability and resistance to degradation. PAN is produced by polymerization of acrylonitrile monomer as shown in Fig. 1, resulting in granulated or powder form.

This powder, in virgin form, has little application in the industry. Therefore, it must be processed with numerous co-monomers into another form by dissolving it in a suitable solvent at room or elevated temperature to form polymer [17]. One such form is polyacrylonitrile fiber. Table 1 highlighted the properties of PAN.

Other properties include resistance to; hydrolysis, acids, alkalis,

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Fig. 1. Polymerization of acrylonitrile (AC) to PAN (17).

oxidation and organic solvents, all these applications show the versatile application of PAN product.

2.1. PAN crystallization

PAN exists in semi-crystalline and amorphous polymers forms. The physical, chemical electrical, mechanical and thermal properties strongly relied on the polymer crystalline structures. Under debates are the crystalline structures and the unit cells of PAN because different polymorph is exhibited by the PAN thermal history [19]. Therefore, some PAN materials are considered brittle in nature, and cannot be reused once it has been processed, thus, further research is needed [20]. Furthermore, it is very important to know that the moisture content has significant effect on the crystallinity because, polymer brittleness intensely relies on the microstructure of the semicrystalline polymers such as PAN. It is very important to further explore, how the crystalline domains of PAN advance with the moisture content on drying. Although, many types of research on crystallization of polymer materials have been investigated [21–29].

Different analytical methods are used to estimate the degree of crystallinity and it usually ranges between 10 and 80%, thus crystallized PAN polymers often exist in semi crystalline according to Bartczak [30]. The properties of semi crystalline polymers are determined by the molecular chain's orientation, the size and the degree of crystallinity [31–34].

Therefore, its crystallinity is an indication of the amount of the crystalline fraction of polymer with respect to the amorphous fraction. This influences the polymer properties such as hardness, modulus, tensile, stiffness, creases and melting point etc. Hence, crystallinity plays a significant role when selecting PAN materials for a particular application [35–39]. In addition, tangled chains and strong intermolecular forces are associated with the large molecules of PAN crystals, PAN does not have a vapour phase, it decomposes before the temperature is sufficient to form vapour. This is the reason why it is difficult for the large crystals establish in the solid phases of smallest molecules to form in PAN [58.39].

Alternatively, amorphous and crystalline phases can be adopted for the modeling of solid polymers [40].

2.2. Recycling of polyacrylonitrile

Polyacrylonitrile is one of the important polymer materials for fibre development broadly because of its lightweight, abrasion resistance, exceptional mechanical properties and good insect repellant resistance etc [41]. This shows that its products usage is on the increase and therefore, generating environmental concern [42,43]. This development led governments around the world to promulgate laws on the reuse and recycle of these materials. Recycling of PAN fiber is a viable option to explore because most of the high-performance fibers used today are produced from polyacrylonitrile as carbon products. Hence, recycling of polyacrylonitrile fibers is thus interesting from both economic and ecological point of view. The adopted ways of recycling used PAN products is posing a challenge for ecological and economic reasons; hence the need to intensify research development into its recycling. This recycling possibility is needed in order to extract valuable material property disposed of as wastes and to solve the environmental related concerns. Therefore, improve developmental research into ways of recycling PAN materials by blending with other polymers could be a good option to explore.

Polyacrylonitrile recycling is a developed technological process that relies on PAN-based products and constrained by a well-established feasible methodology (material separation/blending technique) (Fig. 3), product resources, capital (costs of disposal and processing), human resources and unique market oppositions (competition with virgin materials). In addition, the availability of perfect substitutes in form of virgin materials and difficult processing conditions limits its recycling exploration. Consequently, its recycling processes are delicate area,

Table	1
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Properties of polyacrylonitrile [18].

Polyacrylonitrile (PAN)	Properties
Glass transition temperature	100 °C
Melting temperature	317 °C
Decomposition temperature	175 °C
Amorphous density at 25 °C	1.184 g/cm ³
Molecular weight of repeat unit	53.06 g/mol
Tensile strength	24-65 cN/tex
Moisture content at 20 °C, H.R.	65% (1–2%)
Operating temperature (continuous)	130 °C Max
Operating temperature (Peaks)	135–145 $^\circ \text{C}$ Max



Fig. 2. Process flow diagram of polyacrylonitrile from Acrylonitrile and Methyl acrylate (Minhas Tabraiz 2015).



Fig. 3. Schematic setup of melt extrusion machine suitable and adaptable to PAN blending with other materials (Kruder 1985).

walking the thin line between technological feasibility and economic constraints. Beyond the fragility of the recycling industries, the relative usefulness of recycled polyacrylonitrile materials can be dominated by many other factors. However, the consequences of government legislation on the recycling requirements also have the potential of limiting its recycling processes as those materials facing similar economic conditions [44].

In addition, its high processing temperature also makes the material less attractive to recycling because the polymer contents degrade with blended compounds before the melting temperature of polyacrylonitrile is reached during processing [45]. Therefore, high-value product recovered from PAN recycling depends on the quality of the compounding polymer materials. In conclusion, the important benefits of PAN recycling are reduction of waste generation, less need for landfill and possible development of new products [46–50].

2.3. Adopted methods of polyacrylonitrile recycling

PAN is a thermosetting polymer and it may not be possible to recycle through traditional recycling methods. However, it may be recycled through blending with other polymers to develop different products. It may also be used as a filler to strengthen other polymer products or nanoparticle inclusion for some electrically conductive materials.

Polyacrylonitrile comprises of monomers and acrylonitrile (AN) is a copolymer. PAN, which includes carbon fibers and nanofibers are adopted as the main precursor of carbonaceous materials, is a vital polymeric compound [51–56]. Due to high carbon yield of PAN of up to 56% and its good flexibility, thermal property, and stability, it is mostly functional in many textile, fibers and ultrafiltration membranes unit manufacturing [57-60]. In addition, it as AN-based copolymer has weak mechanical properties compared with other AN-based copolymers [61–66]. To enhance its mechanical properties, some developments such as the reinforcement using nanoparticle materials have been reported in the literature [67-69]. Although reinforcing methods are available to enhance mechanical properties, but subsequently, it presents problems because it reduced biodegradation [70]. Hence, compounding of polyacrylonitrile with another synthetic polymer is seldom compatible due to the strong dipole-dipole nitrile group interactions and the weak van dal Waal bond of its structure [71–75].

In material science, polymer blends have been effectively introduced in order to modify and improve on many polymer properties as required in their applications. The blending methods are theoretically based on the guiding prospect of certain blend properties. This control is done through the amendments of the chemical molecular structures and compositions by means of proper additives and nanoparticles choice. This application was observed in the work of some researchers [76,77]. However, a well-established blend of miscible polymers is very uncommon. Coarse morphology largely is associated with immiscible polymer blends, which sometimes manifested in their poor mechanical properties. However, from immiscible polymers it is possible to achieve a highly dispersed mixture.

2.4. Polyacrylonitrile melts

The transition of polymer from a crystalline or semi-crystalline phase to a solid amorphous phase is regarded as polymer melts. This also applied to polyacrylonitrile materials. For Newtonian fluids, temperature dependent constant is the viscosity, irrespective of the shear rate. Conversely, the viscosity varies with shear rate for non-Newtonian fluids and not only with temperature in polymer melts. The materials resistance to shear flow is called melt shear viscosity [78]. As a whole, polymer melts are highly viscous owing to their long molecular chain structure. Their viscosity conceived as the polymer thickness varies from 2 to 3000 Pas (water 10^{-1} Pas, glass 10^{20} Pas). Hence, in polymer analysis, viscosity is conveyed as the ratio of force per unit area (shear stress) to the rate change of shear strain (shear rate).

2.5. Brief literature survey on polyacrylonitrile

Polyacrylonitrile transforms into carbon at elevated temperature in many processes and it is used as precursor materials for carbon fiber manufacturing as shown in Fig. 2. PAN materials with its good anticorrosion properties when used lose little tensile strength, this allowed it to be used as a replacement for polyester fibres in many applications [79, 80]. Also, its fibre which is a low cost core material has been used as a filter material instead of the chopped strands of the composite mat and the expensive core material of other polymers. In a recent study, research has shown that the mechanical performance of polyacrylonitrile as a core material is more superior to the virgin core material and less costly [81, 82]. In the successfully blended modified PAN and cellulose acetate (CA) [83]. Their findings showed partial miscibility of the blend demonstrated by the inward migration of the two glass transition temperatures (Tg), which was reproducible with the conjugate phase calculations. Unfortunately, owing to the poor economic benefit of processing, this system has not yet been industrialized. In other related studies, fiber-forming PAN was modified with a low quality of amorphous vinyl monomers in

order to achieve improved dye ability and processability [84,85]. This was in continuation of earlier findings and development on modification of the properties of PAN [86,87]. Furthermore, research findings have shown that the effect of externally applied fibre reinforced PAN materials has excellent flexural performance [88–90].

2.6. Research status on polyacrylonitrile

The blends of PAN with other polymers largely depend on adequate processing method and the understanding of the relationship of structural properties of the parent materials as shown in Fig. 3. The variation in the blend properties is the limiting factor in the understanding of polyacrylonitrile blends [91,92]. However, over the years, viable blending methods due to research efforts have evolved by studying the rheology and morphology properties of various blends with polyacrylonitrile as shown in Table 2.

3. Polyacrylonitrile applications

Polyacrylonitrile is attracting much attention and tremendously popular by virtue of its exclusive structure, diversify properties and transformation potential of its structure under extremely high temperature and different applications [120] as discussed in Table 3 below.

3.1. Opportunities and challenges

An outline of the technological advancements linking PAN, its recycling, structure and morphology of blends clearly indicates that this area of knowledge is currently in the light of development at unprecedented rates. Efficiency is the guiding principle behind this progress of PAN functionality. However, effective implementation of its recycling processing methods and blending effects depend directly on the understanding of their behaviour, blending techniques and properties. In this respect, challenges result from its sensitivity to varying factors during production, such as temperature-dependent effects and properties such as mechanical and chemical. Immediate significance problem is the fact that, PAN blends are often dependent on the morphology, rheology, and properties of the material blended certainly, these are considered, basic properties of the materials. These intrinsic properties of PAN blends have the tendency to produce new and unexplored properties, which need to be fully studied and understood for further applications. It is also important to note that most PAN products over a wide range of temperatures perform their dynamic functions in different environments. Their degradation tends to accelerate in such conditions, and their functional applications are consequently altered [155-157]. In addressing the outlined polyacrylonitrile problem areas, experimental investigations are required. Hence, there is the need to further develop the blending process of compatible polyacrylonitrile products for advanced applications. In this regard, it is important to treat its blends as an integral part of polymer science development and technology [158-161]. Predicting PAN products end-use properties is faced with overwhelming challenges such as the prediction of blend output, rheology, and morphology, forming shrinkage, wrappage and stress/strain cracking. These remain unresolved during many PAN processing. Also, the aim of precise property prediction in polyacrylonitrile study is likely to remain a challenge for a considerable length of time. However, the discovery and application of new technologies will play significant roles in its field of development. These include various polyacrylonitrile blends, nanostructured materials with exceptional properties, conductive polyacrylonitrile for electronics, self-assembly processes for the creation of special PAN polymeric structures, developing of smart materials and PAN-based engineering in the field of medicine.

In the immediate future, continuing progress in the field of smart polymers will focus on the intensity of research efforts directed towards the development of polyacrylonitrile blends with enhanced adaptive capabilities. Therefore, due to the mentioned applications and Table 2

Polyacrylonitrile process, contribution and remarks.

Authors	Process	Contribution	Remarks
Anjali & Srivastava. 2003 [93]	Copolymerized Linalool (LIN) and acrylonitrile (AN) using benzoyl peroxide as a crosslinking agent in xylene at 75 °C for 60 min	The TGA data show that the copolymer has a Tg of 50 °C and is highly thermally stable.	The mechanism o copolymerization has been elucidated, showing that with an increase in temperature the rate of copolymerization increases.
Yeo & Kiran 2004 [94]	Copolymerization of acrylonitrile with methyl methacrylate and 2-chlorostyrene in supercritical CO ₂	Morphologies ranging from free- flowing powders to soft solids and gels are obtained, depending on the copolymer composition. Copolymerization and the insertion of small portions of methyl methacrylate or 2- chlorostyrene into the chain significantly altered the morphology of acrylonitrile homopolymer. Inaddition, with increasing comonomer insertion into the chain the degree of agglomeration revealed an increase	Their work showed that, by free-radical precipitation polymerization in supercritical carbon dioxide, the copolymers and homopolymers of acrylonitrile with 2-chlorostyrene and methyl methacrylate can be formed.
Zhong et al., 1997 [95]	Blending. Of acrylonitrile chlorinated polyethylene- styrene copolymer (ACS) with polyvinyl chloride (PVC)	Their study focused on the phase behaviour, miscibility and thermal stability of the blends. The PVC is immiscible with chlorinated polyethylene (CPE) in ACS but partially miscible with SAN in ACS while SAN dissolves more in the PVC phase than it does in the PVC in the SAN phase	A three-phase structure of PVC/ ACS blends was displayed and the interfaces between any two of the three phase are well bonded together.
Camino et al., 2011 [96]	The thermal behaviour of a novolac resin or a resol with blends of nitrile- butadiene rubber (NBR)at the heating range of 200–300 °C	Due to the cyclizing chain reactions and exothermic curing relating to the double bonds of the nitrile groups of its acrylonitrile units and its butadiene units, the NBR became hard and insoluble.	NBR showed compatibility with the novolac and not with the resol Also, because of crosslinking of th rubber and resin, heating increased the modulus of elasticity of the mixtures. Therefore, when the mixture was heated linking of the resin resulted in phase separation in the

of the rubber (continued on next page)

prevented curing

Zou & Pan.

2008 [101]

In the

(ATO)

characterization of

PAN/antimony-

doped tin oxide

nanocomposites

Та

able 2 (continued)				
Research Status	on PAN Blending met	thods		Researc
Authors	Process	Contribution	Remarks	Authors
Blake et al., 2011 [97]	In the study of the fabrication and thick film of marco/nanoscale aggregate characterization and particularly the de-aggregated nanodiamond/ PAN composite	Traces of PAN using the thermogravimetric analysis (TGA), ultra-dispersed PAN/(ox-UDD) and nanodiamond PAN/ (ox-ND) thick films revealed that ox- UDD and ox-ND additives acted as thermally stabilizing fillers.	The development is in line with the PAN matrix cross- linking/improved additive reaction existing in these composite films, with the greatest enhancement observed in the ox-ND composite.	Semsarz & Azi 1997
Agnihotry et al., 2004 [98]	Nanocomposite electrolytes with fumed silica in polymethyl methacrylate (PMMA)	The thermal analysis result illustrated that traces of PMMA used in synthesizing the composite polymer electrolytes (CPEs) at a heating rate of 10 °C/min, resulted in two different weight losses.	the two reaction stages have a comparable weight loss; the first losses stage occurred at low temperature that is endothermic while the other occurring at higher temperature is exothermic.	Bajpai e 2005
Boguslavsky & Margel. 2004 [99]	The synthesis and characterization of polystyrene/ polyacrylonitrile (PS/PAN) composite particles of thin size distribution by a single-step enlargement of unvaried PS template microspheres with methylene chloride emulsion droplets	The work shows a significant shift in the PS decomposition temperature towards higher temperature.	This shift indicates a probable potent interaction between the PAN chain and PS after crystallization.	Naficy e 2012
Pourjavadi & Zohuriaan- Mehr. 2003 [100]	comprising of acrylonitrile (AN) and benzoyl peroxide (BP) The synthesis and thermal characterization of new polysaccharide-g- polyacrylonitrile copolymers	Thermogravimetric study showed that in the first stage the degradation of graft copolymer is very fast and then degrades rather slowly, showing higher thermal stability of the process in the latter stage. In addition, when compared with the	The copolymers were more thermally stable than the corresponding non-grafted substrates, although degradation begins at relatively lower temperatures than the non-grafted counterparts.	Musale Ashwa -Kuma [105] Huang e 2003

corresponding nongrafted substrates the overall thermal stability of all the graft copolymers improved.

The TGA result

shows two curves;

the first curve was

the decarboxylation

of methyl acrylate in

co-PAN caused by

second curve was

weight loss and the

Research Status on PAN Blending methods					
Authors	Process	Contribution	Remarks		
Semsarzadeh, & Azizalah. 1997 [102]	In the thermal reactions and analysis of PAN films	the thermo- oxidative degradation of PAN macromolecular chain due to weight loss. The thermal treatment of the films shows that the weight loss before and after the treatment remains			
Bajpai et al., 2005 [103]	The study of the thermal, morphological and annealed micro hardness characterization of gelatin based interpenetrating network of polyacrylonitrile.	The cross-linking of PAN in an interpenetrating network (IPN) increases with the content of gelatin and the crystallinity also increased with increasing content of acrylonitrile (AN) in the IPN. The result also revealed an optimum temperature of 70 °C for annealing	Gelatine based hard IPNs of PAN can be developed with the use of hydrogels.		
Naficy et al., 2012 [104]	The pH sensitivity and double network hydrogel synthesized of the oligo-monomers of poly (ethylene glycol) methyl ether methacrylate structure, formed as the first polymer network and poly (acrylic acid) as the second	The strong intermolecular interactions between the nonionic groups and the neutral poly (ethylene glycol) side chains offer high sensitivity to pH changes and the hydrogel excellent mechanical strength.	Such a material has artificial controlled release devices because of its sensitivity to pH changes and robust nature.		
Musale and Ashwani -Kumar 2000 [105]	In the study of the pH and solvent resistance of surface cross- linked polyacrylonitrile/ chitosan composite nanofiltration membranes.	Due to the cross- linking, the membrane was stable at pH_{11} than at $pH_{2.5}$. The stability of the pH values increased with increasing glutaraldehyde concentration because of reduced swelling	The nanofiltration membranes possessed solvent recovery potentials and other components of small molecular weights.		
Huang et al., 2003 [106]	Graphene and inorganic/organic double network hydrogel composing of polyacrylic (PAN) acid prepared by two-step synthesis	The first synthesis network is by as- prepared 3D graphene architecture and the second network by the acrylic acid monomer dispersion into the consecutive channels and polymerized. This inorganic-organic double-network hydrogel shows both electrical conductivity and flexibility	These properties may be adopted in the succeeding generation of flexible electric devices.		
Hoffman 2001 [107]	In the hydrogels for biomedical application	By hydrophobic interactions, the hydrogel can be	In the crosslinked state, the hydrogels cross- ntinued on next page)		

The blend method

is more thermally

stable than the

corresponding

polyacrylonitrile

neat

process.

Table 2 (continued)

Table 2 (continued)			Table 2 (continued)				
Research Status	Research Status on PAN Blending methods			Research Status on PAN Blending methods			
Authors	Process	Contribution	Remarks	Authors	Process	Contribution	Remarks
	studied the hydrolysis of PAN to form amide and acid groups from the nitrile groups.	stabilized, thus forming a physical hydrogel if the nitrile groups remain in acceptable concentration and association during	linked reach an equilibrium swelling level in aqueous solutions which depends mainly on the cross-linked density	Qinwu et al., 2010 [113]	The performance of four fibers (polyester, PAN, lignin, and asbestos) on reinforced asphalt concrete was worked on	The asphalt concrete rutting resistance, fatigue life, and toughness was significantly improved by the fibres.	The result shows promising application of polyacrylonitrile in the construction industries.
Latifi et al., 2010 [108]	The electro-spun nanofibers morphology and mechanical properties of PAN/ multi-walled carbon nanotube (PAN/MWNTs) nanocomposite	the process. Result confirms the enhancement of the mechanical properties by increasing MWNTs content in the nanofibers, with a significant improvement over the percolation threshold value of MWNTs in fibers. Their result also shows an	It was revealed that the peaks related to CH ₂ and C—N bonds reduced distinctly during stabilization of Polyacrylonitrile fibers.	Dao et al., 2003 [114]	Worked on. Electrochemically synthesized of polyaniline on carbon PAN aerogel electrodes used as active material in super capacitor devices	Two electrochemical phenomena were detected; the first step depend on double layer electrostatic energy storage of the carbon PAN aerogel/interface solution, and the associated redox processes in polyaniline, for which the potential	Their findings are encouraging and authenticate the essence of a symmetric super capacitor, depend on carbon PAN aerogel, concealed by polymers conduction electrons.
Eslami et al	In the study of	improvement in the tensile modulus of PAN/MWNTs composite, indicating an improved dispersion of MWNTs in the blend. These reductions are	The carbon fibers	Kim et al., 2005 [115]	The work on 2- acrylamido-2- methyl propane sulfonic acid copolymerizing with modified PAN methyl	range depends on the Faradic charge. The findings showed partial miscibility from the two types of modified PAN with CA from the solution blends, as demonstrated by the	Compositions matching Coran- Patel model prediction and the tensile strength minimum.
2009 [109]	Polyacrylonitrile fiber FTIR spectra samples amidst distinctive comonomers	related to the stabilization procedure and cyclization of nitrile groups. From their findings, the reduction in PAN fibers contains an itaconic acid (IA) comonomer, is very intense when compared with PAN fibers contain sodium 2-methyl-2- acrylamidopropane sulfonate comonomer.	made from this process bears greater tensile strength attributed to appropriate stabilization of the nitrile groups.		acrylate (MA) and compounded with cellulose acetate in dimethyl formamide	inward movement of the two Tgs. The migration of Tg was much better with PAN compared to CA, an evidence of greater CA solubility in PAN, a result consistent with the conjugate phase calculations. Their SEM micrographs revealed that at 40/ 60 for AP-PA-CA and 60/40 for MA- PAN-CA blends, phase inversion	
Biedunkiewicz et al., 2011 [110]	Thermo-analytical methods were used to study the oxidation and pyrolysis of PAN in dry air	findings revealed that by controllable means during blending processes the pyrolysis and oxidation of Polyacrylonitrile	Their result is promising and can be explore further.	Peebles and Peters, 1990 [116]	Under the inert atmospheric conditions, the thermal degradation of Polyacrylonitrile	occurred. At prolonged heating at 225 °C, PAN could be transformed into a more stable material	Polyacrylonitrile products are more stable at higher temperature.
Whitb et al., 2012 [111]	High temperature oxidative resistance of PAN methyl methacrylate copolymer powder, during the converting of the copolymer into carbonized	can be conducted. The result shows that chemical and thermal treatments are critical in obtaining porous.	PAN-based carbon monolith shows that the process improved the thermal properties of the copolymer	Zhu et al., 2013 [117] Seydibeyoglu. 2012 [118]	In the study of PAN/poly (Vinyl alcohol) blended film properties. The partial biobased PAN- lignin as a potential carbon fiber precursor	PAN could be introduced into the blend to exert notable effects on the PVA films properties. It is possible to develop a new precursor material with PAN and lignin blend. This also	Polyacrylonitrile has a positive effect as a blended material. Making the Polyacrylonitrile precursor greener and a partially PAN replacement
Mohanty et al., 2001 [112]	monolith Successful modifying of the pineapple leaf fibers by grafting them onto PAN	Improving the pineapple leaf fiber properties was the main focus of the work	This was successful achieved by grafting them onto polyacrylonitrile		blend	demonstrated lignin new application area, which in many different industries is an undervalued co-product.	with a renewable resource is envisioned to boost the world environment.
Under environn	nental temperature an	d water condition stud	ly			(ca	ntinued on next page)

(continued on next page)

Table 2 (continued)

Authors	Process	Contribution	Remarks
Feng et al., 2014 [119]	The thermal and mechanical properties enhancement of PAN through compounding with tea polyphenol (TP)	The research concede that better anti-wear ability can be achieved with PAN/TP blends containing 12.5 wt % TP and similar hardness to those of acrylonitrile butadiene styrene (ABS). In addition, the referenced polymer ABS have a higher impact strength than all the prepared PAN/TP blande	when compared with the pure PAN the blends revealed enhanced thermal stability.

Table 3

Area of application of Polyacrylonitrile material.

S/ N	Industries	Application	5.0	in con
3.1	In automobile industries	Carbon fibers from acrylic precursors such as PAN- based carbon fibers have been extensively used as reinforcing constituents in automobile structures because of its stability. It is also finding applications in thermal and acoustic insulating materials in various automotive components such as the engine compartment insulation. This is due		
3.2	In textile industries	to the fire and heat protective apparel [121]. Copolymers comprising polyacrylonitrile are regularly used as fibers to make knitted clothing such as socks and sweaters, together with outdoor products like tents and similar items. Piece of clothing label showing "acrylic", denote that it is produced from some copolymer of polyacrylonitrile. It was processed into the spun fiber at DuPont in 1941 and marketed under the name of Orlon. Acrylonitrile is usually employed as a componence with styrang (e.g. ASA SAN) and		
3.3	In high temperature industrial plants	as a comonomer with styrene (e.g. ASA, SAN and ABS) [122]. Hot gas filtration systems of most power generating plants have been using homopolymer fibers of polyacrylonitrile. This is used to filter fly ash particles and reduced air pollution in most of the stations [123–129]. PAN is also finding applications in membranes systems in water and chemical treatments because of its good solvent resistance, surface area, antifouling properties, excellent mechanical properties and high porosity [123,126,130,131]. Inaddition, PAN ability to form uniform polymeric interconnected structures that exhibit excellent mechanical properties with high porosity, high electrolyte uptake and good relative absorption ratio make it suitable for the application [120]	3.7	In pac
3.4	In the Aerospace industry	application [129]. Carbon fibers produced from PAN have characteristics properties such as low thermal coefficient of expansion, specific modulus, high specific strength, high thermal stability and high fatigue strength. Inaddition, the produced PAN materials find application in various configurations to reinforce lightweight polymer materials. These make the fibers very attractive to be utilized for composites structural materials fabrication and reinforcing materials in the aerospace industry. This is because the carbon fiber can be stiffer than titanium, stronger than steel and lighter than aluminum and use as a	3.8	In Elec Applic

S /	Industries	Application
Ν		
3.5	In Medicine	nanoparticle in a variety of applications in the industry [132–135]. Polyacrylonitrile materials are having a wide range of applications and replacement for other biomaterials in the medical field. This is because of their unique properties such as light weight, stiffness, high strength, corrosion and resistance to fatigue. The materials are also harmony with the
3.6	In Construction	ratigue. The materials are also harmony with the present-day medical diagnostic devices and had no undesirable consequence in the body system functional operations such as the implants, limbs, components and replacement filler materials, supplement, and body organs fixation [136–138]. Some carbon fiber reinforced polymer (CFRP) made from it are also having applications in ligament, tendon, cartilage, dental post, dental bridges, skull, sterile bandage, bed sore and scars, external fixator for repairing and lengthening bones and also as artificial bones and replacing pieces for different joints [136, 139]. Furthermore, PAN materials from CFRP are used for welfare equipment such as wheelchairs, care beds and portable slope [140,141]. Polyacrylonitrile products in form of carbon fibers are finding application as construction materials, reinforcement and continuous reinforcement materials all over the world. This is because of its important characteristics such as its lightweight, high strength, stiffness, toughness and good durability. Carbon fibers reinforced polymer (CFRP) are used to strengthening and improve structures and sheets on beam surfaces, floors, the building roofs, bridge repair, rebar, grating into concrete, warping around columns, piers and carrying beams of the bridge [142–144]. Inaddition, concrete reinforcement with long and short carbon fibers, suspension bridge cables and PAN fibers as an alternative for steel frames are some of the construction industry polymer applications. In recent years carbon fibers composites are used as buildings reinforcement
3.7	In packaging	materials against natural disasters and weak structures enhancement. Also, it is anticipated that against the electromagnetic inferences CFRP's are used as protecting material and as intelligent material for structures defects detection [144, 145]. Instead of asbestos in structural applications carbon fibers can be used. Research finding has also concluded that better elastic modulus and strength can be achieved with cement having a low percentage of short carbon fibers in comparison with using asbestos as reinforced material. This also has less environmental effects [145]. The U.S. Food and Drug Administration (FDA) has categorized acrylic polymers as nontoxic, approved for materials handling and packaging. Because of their wide property range such as excellent barriers to permeation by gases, organic solvents, transparent, heat resistance, and environmental forces degradation resistance. Acrylic polymers are used in an astounding variety of applications that span the range of domestic, medical, industrial, textile, construction, automotive and furniture industries [146,147].
3.8	In Electrical Application	However, the level of residual monomers are the main concerns with acrylic polymers and the presence of non-acrylic additives which contribute to the material toxicity. As a result, some acrylic latex dispersions can be mild skin or eye irritants. PAN composites are used as a protective layer against electromagnetic interferences and can carry static load. It is also a conducting polymer due to their molecular structure, they have specific properties such as controlled electrical conductivity, simulated electrical properties

(continued on next page)

Table 3 (continued)

S/	Industries	Application
S/ N 3.9	Industries	Application through the tailoring of certain molecular structures, preparation of various nanostructured forms [148,149]. Therefore, it has been successfully used in energy storage device and sensor applications owing to its good mechanical, thermal properties, and its low cost [150–153]. Many sporting goods have made from acrylic material because of carbon fibers superior performance. These ranges from fishing rods, golf shafts, synthetic fields, shoes, shirts, awnings, sails for yachts, squash rackets, baseball bats, badminton, ski sticks and tennis rackets into other sports materials and gears. Today in many sporting roads acphon fibers accomparised an
		vital and essential material for both the indoors and outdoors applications [140,141,154].

availability of pure PAN and recycled materials, it is important to develop and adapt to the existing and newly discovered techniques in the formation of its blends for its developmental applications. On this basis, the unique opportunities offered by the recycling of PAN products will continue to stimulate further technological inquest on new materials. These materials will have application in different sectors of engineering, medicine, manufacturing, military, industrial, smart material and domestic products.

3.2. Correlation of the review

The review focused on Polyacrylonitrile blends and application in Manufacturing Technology: Recycling and Environmental Impact. This is the area we assumed is of immediate concern and needs improvement and support. Although, there is more to learn due to the ongoing development in its application because in the present form, most information on polyacrylonitrile products are in private and patent domain due to the sensitivity of its development information. This review is aimed to guide all sectors into its demand and future prospect. Hence this is to support the research into the improvement and application of the material.

4. Conclusion

This review provides the collection of knowledge based on what has been published in the literature on polyacrylonitrile products. Developments involving its blending, the resulting properties, uses, and applications, vividly show that the field of polyacrylonitrile technology is rapidly developing. Different PAN blends represent different feasible methods for exploiting some of these developments. Some existing blending techniques used in the processing of polymer with focus on polyacrylonitrile have been reviewed in this paper. Future research is expected to focus on combining its properties. This is in order to identify new applications and to focus more on the recycling of the polymers. Furthermore, simulation processes into the combination of polyacrylonitrile development are still needed. This is to predict the performance of PAN materials in different applications, especially in polymer science.

Declaration of competing interest

This serve to notify you that the manuscript is original of the author work and there is no conflict of interest of any kind regarding the manuscript: Review of Polyacrylonitrile Blends and Application in Manufacturing Technology: Recycling and Environmental Impact.

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References

- M. Misson, H. Zhang, B. Jin, Nanobiocatalyst advancements and bioprocessing applications, J. R. Soc. Interface 12 (102) (2015), https://doi.org/10.1098/ rsif.2014.0891.
- [2] K. Müller, et al., Review on the processing and properties of polymer nanocomposites and nanocoatings and their applications in the packaging, automotive and solar energy fields, Nanomaterials 7 (4) (2017) 74, https:// doi.org/10.3390/nano7040074.
- [3] N. Nasee, et al., A novel PAN-GO-SiO2 hybrid membrane for separating oil and water from emulsified mixture, Materials 12 (2) (2019) 1–13, https://doi.org/ 10.3390/ma12020212.
- [4] S.-J. Park, G.-Y. Heo, Carbon Fibers, 2015, https://doi.org/10.1007/978-94-017-9478-7.
- [5] Acrylonitrile and Acrylonitrile Polymers M.M. Wu, Encyclopedia of Polymer Science and Technology, John Wiley & Sons, Inc, 2001, https://doi.org/10.1002/ 0471440264.pst010.
- [6] K. Friedrich, Polymer composites for tribological applications, Advanced Industrial and Engineering Polymer Research 1 (1) (2018) 3–39, https://doi.org/ 10.1016/j.aiepr.2018.05.001. Elsevier Ltd.
- [7] F.H. Isikgora, C.R. Becer, Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers, Polym. Chem. 6 (2015) 4497.
- [8] A.M. Tofail, S. Koumoulos, E.P. Bandyopadhyay, A. Bose, S. O'Donoghue, Lisa, C.A. Charitidis, Additive manufacturing: scientific and technological challenges, market uptake and opportunities, Mater. Today (2017) 21, https://doi.org/ 10.1016/j.mattod.2017.07.001.
- [9] C. Soutis, Carbon fiber reinforced plastics in aircraft construction, Mater. Sci. Eng., A 412 (1) (2005) 171–176.
- [10]] Š. Monika, S.M. Gražyna, B. Karla, Effect of nanofillers dispersion in polymer matrices: a review, Sci. Adv. Mater. 3 (2010) 1–25, https://doi.org/10.1166/ sam.2011.1136.
- [11] O.S.I. Fayomi, O.O. Joseph, I.G. Akande, C.K. Ohiri, K.O. Enechi, N.E. Udoye, Effect of CCBP doping on the multifunctional Al-0.5 Mg-15CCBP superalloy using liquid metallurgy process for advanced application, J. Alloys Compd. 783 (2019) 246–255.
- [12] B.K. Chaudhary, J. Farrell, Preparation and characterization of homopolymer polyacrylonitrile-based fibrous sorbents for arsenic removal, Environ. Eng. Sci. 31 (11) (2014), https://doi.org/10.1089/ees.2014.0169.
- [13] J.J. Ahire1, D.P. Neveling, L.M.T. Dicks, Polyacrylonitrile (PAN) nanofibres spun with copper nanoparticles: an anti-Escherichia coli membrane for water treatment, Appl. Microbiol. Biotechnol. (2018), https://doi.org/10.1007/s00253-018-9051-0.
- [14] S.K. Nataraj, S.K. Yang, T.M. Aminabhavi, Polyacrylonitrile-based nanofibers—a state-of-the-art review, Prog. Polym. Sci. 37 (2012), https://doi.org/10.1016/ j.progpolymsci.2011.07.001.
- [15] S. Khademolqorani, A.Z. Hamadani, H. Tavanai, Response surface modelling of electrosprayed polyacrylonitrile nanoparticle size, J. Nanoparticles 2014 (2014) 7, https://doi.org/10.1155/2014/146218. Article ID 146218.
- [16] M. Ma, C. Zhang, G. Huang, B. Xing, Y. Duan, X. Wang, Z. Yang, C. Zhang, Synthesis and electrochemical performance of polyacrylonitrile carbon nanostructure microspheres for supercapacitor application, J. Nanomater. 16 (1) (2015) 1, https://doi.org/10.1155/2015/246093. Article 269.
- [17] H. Ma, H. Qiu, S. Qi, Electrically conductive adhesives based on acrylate resin filled with silver-plated graphite nanosheets and carbon nanotubes, J. Adhes. Sci. Technol. 29 (20) (2015) 2233–2244, https://doi.org/10.1080/ 01694243.2015.1061905.
- [18] Q.-Y. Wu, X.-N. Chen, L.-S. Wan, Z.-K. Xu, Interactions between polyacrylonitrile and solvents: density functional theory study and two-dimensional infrared correlation analysis, J. Phys. Chem. B 116 (28) (2012) 8321–8330, https:// doi.org/10.1021/jp304167f.
- [19] P. Bajaj, D.K. Paliwal, A.K. Gupta, Influence of metal ions on structure and properties of acrylic fibers, J. Appl. Polym. Sci. 67 (1998) 1647–1659.
- [20] M.A. Masuelli, Introduction of Fibre-Reinforced Polymers Polymers and Composites: Concepts, Properties and Processes, 2013, https://doi.org/10.5772/ 54629.
- [21] Z. Zhu, Development of Self-Assembled Polyelectrolyte Membranes for Pervaporation Applications. A Thesis Presented to the University of Waterloo in Fulfillment of the Thesis Requirement for the Degree of Doctor of Philosophy in Chemical Engineering Waterloo, 2006 (Ontario, Canada).
- [22] L. Tan, H. Chen, D. Pan, N. Pan Investigation into the gelation and crystallization of Polyacrylonitrile, Eur. Polym. J. 45 (5) (2009) 1617–1624, https://doi.org/ 10.1016/j.eurpolymj.2008.12.006.
- [23] R. Chiang, Crystallization and melting behavior of polyacrylonitrile, J. Polym. Sci. - Part A Gen. Pap. 1 (1963) 2765–2775.
- [24] L. Zhang, Y. Dai, Y. Kai, R.-G. Jin, Structural evolution and kinetic study of high isotacticity poly(acrylonitrile) during isothermal pre-oxidation, Carbon Letters 12 (4) (2011) 229–235. http://carbonlett.org/10.5714/CL.2011.12.4.229.
- [25] J.W. Hendrix, R. Szeto, T. Nosker, J. Lynch-Branzoi, T.J. Emge, Evaluation of exfoliated graphite to graphene in polyamide 66 using novel high shear

elongational flow, Poly 10 (2018) 1399, https://doi.org/10.3390/ polym10121399.

- [26] M.P. Maitz, Applications of synthetic polymers in clinical medicine, Biosurface and Biotribology 1 (2015) 161–176, https://doi.org/10.1016/j.bsbt.2015.08.002.
- [27] X. Huang, Fabrication and properties of carbon fibers, Materials 2 (4) (2009) 2369–2403, https://doi.org/10.3390/ma2042369.
- [28] M.-H. Kim, C.J. Glinka, S.A. Grot, W.G. Grot, SANS study of the effects of water vapor sorption on the nanoscale structure of perfluorinated sulfonic acid (NAFION) membranes, J. Macromol. 39 (2006) 4775–4787.
- [29] C. Simari, E. Lufrano, L. Coppola, I. Nicotera, Composite gel polymer electrolytes based on organo-modified nanoclays: investigation on lithium-ion transport and mechanical properties, Membranes 8 (3) (2018) 69, https://doi.org/10.3390/ membranes8030069.
- [30] Laguna Hills, CA, US S.-L. Yang, Biocompatible Polymeric Compositions Having Microcrystalline and Amorphous Components and Methods for Their Manufacture United States Unicare Biomedical, Inc., Laguna Hills, CA, US, 2015, p. 8992949, http://www.freepatentsonline.com/8992949.html.
- [31] Z. Bartczak, Deformation of semicrystalline polymers the contribution of crystalline and amorphous phases, Polimery 62 (2017), https://doi.org/ 10.14314/polimery.2017.787 nr11–12.
- [32] M. Walczak, Role and properties of the confined amorphous phase of polymers. Other. Ecole nationale supérieure d'arts et métiers - ENSAM, English, NNT, 2012. ENAM0042>. <pastel-00839174>.
- [33] H. Ogawa, Architectural application of carbon fibers development of new carbon fiber reinforced glulam, Carbon 38 (2000) 211, https://doi.org/10.1016/s0008-6223(99)00146-3.
- [34] M.S.A. Rahaman, A.F. Ismail, A. Mustafa, A review of heat treatment on polyacrylonitrile fiber, J. Poly. Degraded Stability. 92 (2007) 1421, https:// doi.org/10.1016/j.polymdegradstab.2007.03.023.
- [35] T. Mikolajczyk, S. Rabiej, G. Szparaga, M. Boguń, A. Fraczek-Szczypta, S. Błażewicz, Strength properties of polyacrylonitrile (PAN) fibres modified with carbon nanotubes with respect to their porous and supramolecular structure, Fibres Text. East. Eur. 17 (No. 6) (2009) 13–20, 77.
- [36] Z. Song, X. Hou, L. Zhang, S. Wu, Enhancing crystallinity and orientation by hotstretching to improve the mechanical properties of electrospun partially aligned polyacrylonitrile (PAN) nanocomposites, Materials 4 (2011) 621–632, https:// doi.org/10.3390/ma4040621.
- [37] S.F. Fennessey, R.J. Farris, Fabrication of aligned and molecularly oriented electrospun polyacrylonitrile nanofibers and the mechanical behavior of their twisted yarns, Polym. J. 45 (2004) 4217–4225.
- [38] Y. Xu, J. Sun, H. Chen, L. Bai., Synthesis of Polyacrylonitrile by Reversible-Deactivation Radical Polymerization and its Application as Electrode Materials for Electrochemical Double Layer Capacitors. Royal society of chemistry advances.
- [39] Y. Zhang, K. Song, J. Meng, M.L. Minus, Tailoring polyacrylonitrile interfacial morphological structure by crystallization in the presence of single-wall carbon nanotubes, ACS Appl. Mater. Interfaces 5 (3) (2013) 807–814, https://doi.org/ 10.1021/am302382m.
- [40] G.L. Collins, N.W. Thomas, G.E. Williams, Kinetic relationships between heat generation and nitrile consumption in the reaction of poly (acrylonitrile) in the air at 265°C, Carbon 26 (1988) 671, https://doi.org/10.1016/0008-6223 (88)90070x
- [41] W. Pan, S.L. Yang, M.J. Jian, G. Li, Electrical and structural analysis of conductive Polyaniline/polyacrylonitrile composites, Eur. Polym. J. 41 (2005) 2127–2133.
- [42] H. Gunerhan, S. Agi, Energy-environment-city triangle, Energy Sources, Part A Recovery, Util. Environ. Eff. 26 (7) (2004) 697–706, https://doi.org/10.1080/ 00908310490445535, 0 10.1080/00908310490445535.
- [43] B. Zhang, H. Misak, P. Dhanasekaran, D. Kalla, R. Asmatulu, Environmental impacts of nanotechnology and its products, in: Proceedings of the 2011 Midwest Section Conference of the American Society for Engineering Education, vol. 1, 2016, pp. 1–9.
- [44] S. Mahalingam, X. Wu, M. Edirisinghe, Evolution of self-generating porous microstructures in polyacrylonitrile-cellulose acetate blend fibers, Journal of Materials and Design 134 (2017) 259–271, https://doi.org/10.1016/ j.matdes.2017.07.050.
- [45] P.C. Rader, F.R. Stockel, Polymer Recycling: an Overview, Downloaded by Tshwane Univ of Technology on May 23, 2011, 1995 http://pubs.acs.org | doi: 10.1021/bk-1995-0609.ch001.
- [46] D.M. Mousdale, BIOFUELS Biotechnology, Chemistry, and Sustainable Development CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, 2008, pp. 33487–42742. FL -13: 978-1-4200-5124-7.
- [47] L.H.A. Cândido, D.B. Ferreira, W. Kindlein Júnior, R. Demori, R.S. Mauler Recycling cycle of materials applied to acrylonitrile-butadiene-styrene/ policarbonate blends with styrenebutadiene-styrene copolymer addition, in: AIP Conference Proceedings, vol. 1593, 2014, p. 658, https://doi.org/10.1063/ 1.4873865.
- [48] R. Eslami Farsani, R. Fazaeli, Applications of carbon fibers produced from polyacrylonitrile fibers, World Academy of Science, Engineering and Technology International Journal of Structural and Construction Engineering 6 (8) (2012).
- [49] M.R. Buchmeiser, Polymeric Materials in Organic Synthesis and Catalysis, Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim, 2003, 3527306307.
- [50] A. Lim, M.-H. Song, C.-W. Cho, Y.-S. Yun, Development of surface-modified polyacrylonitrile fibers and their selective sorption behavior of precious metals, Appl. Sci. 6 (2016) 378, https://doi.org/10.3390/app6120378.
- [51] S.I. Yoon, S. Kim, C.W. Cho, Y.S. Yun, The preparation of modified industrial waste polyacrylonitrile for the adsorptive recovery of Pt (IV) from acidic solutions, Materials 9 (12) (2016) 988, https://doi.org/10.3390/ma9120988.

- [52] N. Abdul-Munajat, A.H. Nurfaizey, M. Haizal, M.H. Mohd-Husin, S. Hajar-Sheikh, S. Sheikh Md Fadzullah, G. Omar, M. Azli Salim, P. Akademia Baru, The effects of different carbonization temperatures on the properties of electrospun carbon nanofibre from polyacrylonitrile (PAN) precursor, J. Adv. Research in Fluid Mechanics and Thermal Sci. 49 (2018) 85–91.
- [53] N.A. Munajat, A.H. Nurfaizey, M.H.M. Husin, S. H. Sheikh Md Fadzullah, G. Omar, M.A. Salim, The effects of different carbonization temperatures on the properties of electrospun carbon nanofibre from polyacrylonitrile (PAN) precursor, J. Adv. Research in Fluid Mechanics and Thermal Sci. 49 (2) (2018) 85–91. ISSN: 2289-7879.
- [54] I.M. Alarifi, W.S. Khan, R. Asmatulu, Synthesis of electrospun polyacrylonitrilederived carbon fibers and comparison of properties with bulk form, PloS One 13 (8) (2018), e0201345, https://doi.org/10.1371/journal.pone.0201345.
- [55] H.-M. Lee, H.-G. Kim, K.-H. An, B.-J. Kim, Effects of pore structures on electrochemical behaviors of polyacrylonitrile-based activated carbon nanofibers by carbon dioxide activation, Carbon Letters 15 (1) (2014) 71–76, https:// doi.org/10.5714/CL.2014.15.1.071.
- [56] Y. Han, R. Li, C. Brückner, T.M., Vadas controlling the surface oxygen groups of polyacrylonitrile-based carbon nanofiber membranes while limiting fiber degradation, J. Carbon Research. 4 (2018) 40, https://doi.org/10.3390/ c4030040.
- [57] Y. Han, Tailoring Electrospun Carbon Nanofiber Properties for Improving Chemical Sorption, Doctoral-Dissertations.1998, 2018, https://opencommons.uco nn.edu/dissertations/1998.
- [58] M. de Cazes, R. Abejón, M.-P. Belleville, S.-M. José, Review membrane bioprocesses for pharmaceutical micropollutant removal from waters, Membrane J. 4 (2014) 692–729, 10.3390/membranes 4040692.
- [59] B. Fryczkowska, Z. Piprek, M. Sieradzka, R. Fryczkowski, J. Janicki, Preparation and properties of composite PAN/PANI membranes, International Journal of Polymer Science Volume 2017 (2017) 14, https://doi.org/10.1155/2017/ 3257043. Article ID 3257043.
- [60] Y. Qin, H. Yang, Z. Xu, F. Li, Surface modification of polyacrylonitrile membrane by chemical reaction and physical coating: comparison between static and poreflowing procedures, ACS Omega 3 (4) (2018) 4231–4241, https://doi.org/ 10.1021/acsomega.7b02094.
- [61] D. Godshall, P. Rangarajan, D.G. Bairda, G.L. Wilkes, V.A. Bhanu, J.E. McGrath, Incorporation of methyl acrylate in acrylonitrile-based copolymers: effects on melting behavior, J. Polytech. 44 (2003) 4221–4228.
- [62] J.D. Moskowitz, Polyacrylonitrile copolymers: effects of molecular weight, polydispersity, composition, and sequencing on thermal ring-closing stabilization, Dissertations 173 (2015). https://aquila.usm.edu/dissertations/173.
- [63] M.-A. Kim, J. Dawon, T. Syogo, C.-S. Rodolfo, J. Hanlk, C.K. Hwan, L. Sungho, E. Morinobu, Strengthened PAN-based carbon fibers obtained by slow heating rate carbonization, Sci. Rep. 6 (2016) 22988, https://doi.org/10.1038/srep22988.
- [64] G. Ramasubramanian, Influence of Lignin Modification on PAN-Lignin Copolymers as Potential Carbon Fiber Precursors, Graduate Theses and Dissertations.13438, 2013, https://lib.dr.iastate.edu/etd/13438.
- [65] P.R. Lewis, P. Rhys, R. Ken, G. Colin, Forensic Materials Engineering: Case Study, CRC Press, Boca Raton, 2004, 0-8493-1182-9.
- [66] D.C. Wright, Environmental Stress Cracking of Plastics, RAPRA, 2001, 978-1859570647.
- [67] M. Heydari, N. Mohammadi, The cyclization index and toughness of gel spun polyacrylonitrile (PAN) proportionality with its heat of stabilization, Iran. Polym. J. (Engl. Ed.) 27 (2018) 395–404, https://doi.org/10.1007/s13726-018-0617-6.
- [68] F. Mehrpouya, J. Foroughi, S. Naficy, J.M. Razal, M. Naebe, Nanostructured electrospun hybrid graphene/polyacrylonitrile yarns, J. Nanomater. 7 (2017) 293, https://doi.org/10.3390/nano7100293.
- [69] R. Casati, M. Vedani, A review: metal matrix composites reinforced by NanoParticles, J. Metals. 4 (2014) 65–83, https://doi.org/10.3390/met4010065.
 [70] B.K. Kim, Y.S. Oh, Y.M. Lee, L.K. Yoon, S. Lee, Modified polyacrylonitrile blends
- with cellulose acetate: blend properties, J. Polytech. 41 (2000) 385–390. [71] C. Park, Z. Ounaies, J. Su, J.R.J.G. Smith, J.S. Harrison, in: Zhang, et al. (Eds.)
- [71] C. Park, Z. Ounaies, J. Su, J.R.J.G. Smith, J.S. Harrison, in: Zhang, et al. (Eds.), Polarization Stability of Amorphous Piezoelectric Polyimides, Materials Research Society Proceedings: Electroactive Polymers, 1999, p. 600.
- [72] T.A. Adegbola, E.R. Sadiku, S.S. Ray, Atomic force microscopy and tensile strength analyses of recycled PAN and PET blends, Int. J. Environ. Monit. Anal. 3 (5–1) (2015) 17–21, https://doi.org/10.11648/j.ijema.s.2015030501.13. ISSN: 2328-7659 (Print). ISSN: 2328-7667 (Online).
- [73] I. Rosales-Candela, J. Soto-Bernal, R. González-Mota, J.T. Vega-Durán, A. Bonilla-Petriciolet, Attainment of the Absorption Spectra of Polyacrylonitrile, Based on the AM1 Semiempirical Hartree-Fock Model, Adrian Bonilla-Petriciolet, 2007, p. 6422, https://doi.org/10.1117/12.742351, art. no. 64221E.
- [74] H.D. Johnson, Synthesis, characterization, processing and physical behavior of melt-processible acrylonitrile Co- and terpolymers for carbon fibers: effect of synthetic variables on copolymer structure, Thesis Submitted to the Faculty of the Virginia Polytechnic Institute and State University In partial fulfillment of the requirements for the degree of Masters of Sci. in Macromolecular Sci. and Eng. (2006).
- [75] M. Othman, A. Aschi, A. Gharbi, Polyacrylic acids-bovine serum albumin complexation: structure and dynamics, Mater. Sci. Eng. C 58 (2016) 316–323, https://doi.org/10.1016/j.msec.2015.08.057.
- [76] M. Müller, B. Keßler, J. Fröhlich, S. Poeschla, B. Torger, Polyelectrolyte complex nanoparticles of poly (ethyleneimine) and poly (acrylic acid): preparation and applications, Poly 3 (2011) 762–778, https://doi.org/10.3390/polym3020762. ISSN 2073-4360.

- [77] H. Heinz, C. Pramanik, O. Heinz, Y. Ding, R.K. Mishra, D. Marchon, R.J. Flatt, I. Estrela-Lopis, J. Llop, S. Moya, R.F. Ziolo, Nanoparticle decoration with surfactants: molecular interactions, assembly, and applications, Surf. Sci. Rep. 72 (1) (2017) 1–58, https://doi.org/10.1016/j.surfrep.2017.02.001. ISSN0167-5729.
- [78] L. Yu, Biodegradable Polymer Blends and Composites from Renewable Resources, Copyright by John Wiley & Sons, Inc. All rights reserved. Published by John Wiley & Sons, Inc., Hoboken, New Jersey, 2009 (Published simultaneously in Canada).
- [79] P.C. Almenara, P. Thornburrow, A new glass fiber reinforcement for anti-corrosion composites, in: L.C. Hollaway, M.K. Chryssanthopoulos, S.S.J. Moy (Eds.), Proceedings of the ACIC Conference. 'Advanced Polymer Composites for Structural Applications in Construction', Woodhead Publishing Ltd., Cambridge, Uk, 2004.
- [80] D.K. Sharma, J. Shen, F. Li, Reinforcement of Nafion into Polyacrylonitrile (PAN) to fabricate them into nanofiber mats by electrospinning: characterization of enhanced mechanical and adsorption properties, RSC Adv. 4 (2014) 39110–39117, https://doi.org/10.1039/C4RA05103C.
- [81] C. Hong, J. Han, X. Zhag, Novel phenolic impregnated 3-D fine-woven pierced carbon fabric composites: microstructure and ablation behavior, Composites B 43 (5) (2012) 2389–2394.
- [82] J. Wang, L. Schlagenhauf, A. Setyan, Transformation of the released asbestos, carbon fibers and carbon nanotubes from composite materials and the changes of their potential health impacts, J. Nanobiotechnol. 15 (1) (2017) 1.
- [83] K.K. Byung, Y.S. Oh, Y.M. Lee, L.K. Yoon, S. Lee, Modified polyacrylonitrile blends with cellulose acetate: blend properties, J. Polytech. 41 (2000) 385–390.
- [84] A.K. Gupta, R.P. Singhal, V.K. Bajaj, Aguvwal, Effect of copolymerization with methacrylonitrile on the dielectric relaxation of polyacrylonitrile, J. Appl. Polym. Sci. 28 (3) (1983) 1167–1177.
- [85] P.I. Dalven, J.R. Hilderbandt, A.J. Laccetti, L.T. Hodgins, H.P. Gregor, Acrylonitrile- based copolymers: synthesis, characterization, and formation of ultrafiltration membranes utilized for the immobilization of proteins, J. Appl. Polym. Sci. 30 (3) (1985) 1113–1132.
- [86] Y.S. Oh, S.R. Kim, S. Lee, B.K.J. Kim, Solution blends of polyacrylonitrile with segmented polyurethanes: effect of soft segment, J. Macromol. Sci., Part B – Physics. 34 (3) (1995) 199–214.
- [87] Y.S. Oh, B.K. Kim, Cross linking of Polyacrylonitrile using NCO terminated Urethanes 38 (20) (1997) 5211–5216.
- [88] B.-H. Ji, C.-G. Wang, Y.-X. Wang, Effect of jet stretch on polyacrylonitrile as-spun, J. Appl. Polym. Sci. 103 (5) (2007) 3348–3352.
- [89] S. Wu, F. Zhang, X. Hou, X. Yang, Stretching-induced orientation for improving the mechanical properties of electrospun polyacrylonitrile nanofiber sheet, J. Adv. Mater. Research. 47 (50) (2008) 1169–1172.
- [90] L.-M. Chen, Z. Hong, G. Li, Y. Yang, Recent progress in polymer solar cells: manipulation of polymer: fullerene morphology and the formation of efficient inverted polymer solar cells, J. Adv. Mater. 21 (2009) 1434–1449, https:// doi.org/10.1002/adma.200802854.
- [91] A.E. Naaman, S.M. Jeong, Structural ductility of concrete beams prestressed with FRP tendons, in: Non-Metallic (FRP) Reinforcement for Concrete Structures, Proceedings of the Second International RILEM Symposium (FRPRCS-2), E&FN Spon, London, 1995.
- [92] X. Hou, X. Yang, L. Zhang, E. Waclawik, S. Wu, Stretching-induced crystallinity and orientation to improve the mechanical properties of electrospun PAN nanocomposites, Mater. Des. 31 (4) (2010) 1726–1730.
- [93] S.A. Anjali, A.K. Srivastava, Kinetics and mechanism of copolymerization of linalool with acrylonitrile, J. Macromol. Sci., Pure Appl. Chem. 40 (1) (2003) 61–80.
- [94] S.-D. Yeo, E. Kiran, Copolymerization of acrylonitrile with methyl methacrylate and 2-chlorostyrene in supercritical CO2, J. Macromol. 37 (2004) 8239–8248.
- [95] Z. Zhong, S. Zheng, K. Yang, Q. Guo, Blends of poly (vinyl chloride) with acrylonitrile- chlorinated polyethylene-styrene copolymer. I. Miscibility, phase behavior, and thermal properties, J. Macromol. Sci. Part B: Phy. 36 (4) (1997) 441–454.
- [96] G. Camino, E. Alba, P. Buonfico, K. Vikoulov, Thermal behaviour of elastomerresin mixtures used as friction materials, J. Appl. Polym. Sci. 82 (2001) 1346–1351.
- [97] T.B. Blake, M.A. Seif, J.L. Davidson, C.M. Lukehart, Fabrication and macro/ nanoscale characterization of aggregated and highly de-aggregated nanodiamond/ polyacrylonitrile composite thick films, J. Mater. Chem. 21 (2011) 18832.
- [98] S.A. Agnihotry, S. Ahmad, A. Ahmad, Nanocomposite electrolytes with fumed silica in poly (methylmethacrylate): thermal, rheological and conductivity studies, J. Power Sources 140 (2004) 151–156.
- [99] L. Boguslavsky, S. Margel, Synthesis and characterization of micrometer-sized Homo and composite polyacrylonitrile particles of narrow size distribution on the basis of single-step swelling of uniform polystyrene template microspheres, J. Polym. Sci. Polym. Chem. 42 (2004) 4847–4861. Wiley Periodicals, Inc.
- [100] A. Pourjavadi, M.J. Zohuriaan-Mehr, New polysaccharide-g-polyacrylonitrile copolymers: synthesis and thermal characterization, polymers for advanced technologies, Polym. Adv. Technol. 14 (2003) 508–516.
- [101] H. Zou, W. Pan, Characterization of PAN/ATO nanocomposites prepared by solution blending, Indian Academy of Science. Bull. Mater. Sci. 31 (5) (2008).
- [102] A.M. Semsarzadeh, M. Azizalah, Thermal reactions and analysis of polyacrylonitrile films, Iran. Polym. J. (Engl. Ed.) 1 (2) (1997).
- [103] A.K. Bajpai, R. Bajpai, S. Rajvaisa, Morphological, thermal and annealed microhardness characterization of gelatin based interpenetrating network of polyacrylonitrile: a hard biopolymer, Bull. Mater. Sci. 28 (6) (2005) 529–534.

- [104] S. Naficy, J.M. Razal, P.G. Whitten, G.G. Wallace, G.M. Spinks, A pH-sensitive, strong double-network hydrogel: poly (ethylene glycol) methyl ether methacrylates–poly (acrylic acid), J. Polym. Sci. B Polym. Phys. 50 (2012) 423–430.
- [105] D.A. Musale, A.A. Kumar, Solvent and pH resistance of surface crosslinked chitosan/poly (acrylonitrile) composite nanofiltration membranes, J. Appl.Poly. Sci. 77 (8) (2000) 1782–1793.
- [106] P. Huang, W. Chen, L. Yan, An inorganic-organic double network hydrogel of graphene and polymer, Nano 5 (2003) 6034–6039.
- [107] S.A. Hoffman, Hydrogels for biomedical applications, Adv. Drug Deliv. Rev. 54 (2001) 2–12.
- [108] M. Latifi, M. Yousefzadah, M. Amani-Tehran, Ramakrishan. Morphology and Mechanical Properties of Polyacrylonitrile/multiwalled Carbon Nanotube (PAN/ MWNTs) Nanocomposite Electrospun Nanofibers, 2010.
- [109] F.R. Eslami, S. Raissi, A. Shokuhfar, A. Sedghi, FT-IR Study of Stabilized PAN Fibers for Fabrication of Carbon Fibers, World Academy of Sci., Eng. and Tech, 2009.
- [110] A. Biedunkiewicz, P. Figiel, M. Sabara, Pyrolysis and oxidation of PAN in dry air. Thermo analytical methods, Mater. Sci. 17 (1) (2011). ISSN 1392–1320.
- [111] R.L.D. Whitb, A.V. Korobeinyk, S.V. Mikhalovsky, High temperature oxidative resistance of polyacrylonitrile-methyl methacrylate copolymer powder converting to a carbonized monolith, Eur. Polym. J. 48 (2012) 97–104.
- [112] A.K. Mohanty, P.C. Tripathy, M. Misra, S. Parija, S. Sahoo, Studies on the effect of chemical modification of pineapple leaf fibre by graft copolymerization of acrylonitrile, J. Appl. Polym. Sci. 77 (2001) 3035–3043.
- [113] X. Qinwu, H. Chen, J.A. Prozzi, Performance of fibre reinforced asphalt concrete under environmental temperature and water effects, J. Constr. and Build. Mater. 24 (10) (2010) 2003–2010.
- [114] L.H. Dao, H. Talbi, P.E. Just, Electro-polymerization of aniline on carbonized polyacrylonitrile aerogel electrodes: applications for super capacitors, J. Appl. Electrochem. 33 (2003) 465–473.
- [115] B.K. Kim, Y.S. Oh, Y.M. Lee, K.Y. Lee, L. Soo, Modified polyacrylonitrile blends with cellulose acetate: blend properties, J. Polytech. 41 (2005) 385–390.
- [116] L. JR, H Peebles, W. Peters, A. Snow, P. Peyser, On the exotherm of polyacrylonitrile: pyrolysis of the homopolymer under inert conditions, Carbon 28 (5) (1990) 707–715.
- [117] G. Zhu, F. Wang, K. Xu, Q. Gao, Y. Liu, Study on properties of Poly (vinyl alcohol)/ Polyacrylonitrile blend film, Polímeros 23 (2) (2010) 146–151.
- [118] M.O. Seydibeyoglu, A novel partially biobased PAN-Lignin blend as a potential carbon fiber precursor, J. Biomed. Biotechnol. 2012 (2012) 8, https://doi.org/ 10.1155/2012/598324. Article ID 598324.
- [119] L. Feng, J.-F. Li, J.-R. Ye, W. Song, J. Jia, Q. Shen, Enhancing the mechanical and thermal properties of Polyacrylonitrile through blending with tea polyphenol, J. Appl. Polym. Sci. (2014), https://doi.org/10.1002/APP.40411.
- [120] T.V. Semenistaya, Polyacrylonitrile-based materials: properties, methods and applications, in: I. Parinov, S.H. Chang, V. Topolov (Eds.), Adv. Mater. Springer Proceedings in Physics, Springer, Cham, 2016, p. 175.
- [121] S. Bourbigot, X. Flambard, Heat resistance and flammability of high performance fibres: a review, Fire Mater. 26 (2002) 155–168, https://doi.org/10.1002/ fam.799.
- [122] A. K Haghi, S. Thomas, A. Pourhashemi, A. Hamrang, E. Klodzinska, Nanomaterials and Nanotechnology for Composites: Design, Simulation and Applications, Apple Academic Press, 2015.
- [123] B. Jung, J. Membr. Sci. 229 (2004) 129.
- [124] J.C. Ge, Zi J. Wang, M.S. Kim, N.J. Choi, VOCA air pollutant cleaning with polyacrylonitrile/fly ash nanocomposite electrospun nanofibrous membranes, in: IOP Conf. Series: Materials Science and Engineering, vol. 301, 2018, 012036, https://doi.org/10.1088/1757-899X/301/1/012036.
- [125] J.C. Ge, S.K. Yoon, N.J. Choi, Application of fly ash as an adsorbent for removal of air and water pollutants, J. Appl. Sci. 8 (2018) 1116, https://doi.org/10.3390/ app8071116.
- [126] L. Jing, K. Shim, C.Y. Toe, T. Fang, C. Zhao, R. Amal, K.-N. Sun, J.H. Ho, Y.H. Ng, Electrospun Polyacrylonitrile-Ionic Liquid Nanofibers for Superior PM2.5 Capture Capacity, ACS applied materials & interfaces, 2016, p. 8, 10.1021/ acsami.5b12313.
- [127] M. Manousakas, K. Eleftheriadis, H. Papaefthymiou, Characterization of PM₁₀ sources and ambient air concentration levels at megalopolis city (southern Greece) located in the vicinity of lignite-fired plants, Aerosol and Air Quality Research 13 (2013) 804–817, https://doi.org/10.4209/aaqr.2012.09.0239.
- [128] G. Zhang, H. Meng, Ji Sh, Desalination 242 (2009) 313.
- [129] N. Mariappan, V. Ethirajan, C.A. Murrugesan, Spatio-temporal assessment of air pollution from thermal stations and vehicular pollution from urban places in Tamil nadu, International Journal of ChemTech Research 5 (2013) 172–179.
- [130] N.A. El-Ghamaz, M.A. Diab, MSh Zoromba, A.Z. El-Sonbati, O. El-Shahat, Solid State Sci. 24 (2013) 140.
- [131] X. Dong, L. Ma, M. Chen, L. Zhu, C. Wang, F. Yang, Y. Dong, Fabrication and water treatment application of carbon nanotubes (CNTs)-Based composite membranes, A Rev.. Memb. 7 (1) (2017), https://doi.org/10.3390/membranes7010016.
- [132] R. Eslami Farsani, R. Fazael, Applications of carbon fibers produced from polyacrylonitrile fibers, Inter. J. Chem., Molec., Nucl., Mater. and Metall. Eng. 6 (8) (2012).
- B. Pooja, G. Alka, Carbon fibres: production, properties and potential use, Material Science Research India 14 (2017) 52–57, https://doi.org/10.13005/msri/140109.
 K. Shirvanimoghaddam, S.U. Hamim, M.K. Akbari, S.M. Fakhrhoseini,
 - 34] K. Shirvanimoghaddam, S.U. Hamim, M.K. Akbari, S.M. Fakhrhoseini, H. Khayyam, A.H. Pakseresht, E. Ghasali, M. Zabet, K.S. Munir, S. Jia, J.P. Davim, M. Naebe, Carbon fiber reinforced metal matrix composites: fabrication processes

and properties, Compos. Appl. Sci. Manuf. 92 (2017) 70–96, https://doi.org/ 10.1016/j.compositesa.2016.10.032.

- [135] G. Savage, Carbon-Carbon Composite Materials, Metals and Mater, 1988.
- [136] R.E. Farsani, A. Shokuhfar, A. Sedghi, Carbon fibers-polymer composites in human body, in: E-MRS 2004, Fall Meeting, 2004, pp. 6–10. Warsaw, Poland.
- [137] M.N. Helmus, Overview of biomedical materials, MRS Bull. 16 (9) (1991) 33–38.
 [138] S.R. Pollack, Biomedical Materials: an Overview- Encyclopedia of Mater. Sci. & Eng, 1Pergamon Press, 1986, p. 343349.
- [139] S. Ramakrishna, et al., Biomedical application of polymer composite materials, Compos. Sci. Technol. 61 (9) (2001) 1189–1224.
- [140] P.J. Walsh, Carbon fibers, ASM Handbook, Composites 21 (2001) 35–40. ASM International.
- [141] W.C. Rice, Economics of solid rocket booster for space shuttle, Acta Astronaut. 6 (12) (1979) 1685–1694.
- [142] U. Meier, Carbon fibre reinforced polymers: modern materials in bridge engineering, Struct. Eng. Int. 1 (1992).
- [143] M.A. Ali, et al., Carbon fibre reinforcement of cement, Cement Concr. Res. 2 (1972) 201–212.
- [144] D.D.L. Chung, Cement reinforced with short carbon fibers: a multifunctional material, Compos. B Eng. 31 (2000) 511–526.
- [145] K. Flaga, Advances in materials applied in civil engineering, J. Mater. Process. Technol. 106 (2000) 173–183.
- [146] E.L. Miller, in: In SPE National Technical Conference: Plastics in Packaging and Acrylonitrile—A Dual Meeting, vols. 13–15, 1978, pp. 2231–2261. Chicago, Ill., Nov.
- [147] S. Woods, Candian Packaging 39 (9) (1986) 48.
- [148] T. Semenistaya, N. Plugotarenko, V. Petrov, Appl. Mech. Mater. 727–728 (2015) 145.

- [149] A.N. Korolev, T.V. Semenistaya, I.S. Al-Hadrami, T.P. Loginova, M. Bruns, Perspect. Mater. 5 (2010) 52 (In Russian).
- [150] H. Zheng, H. Xue, Y. Zhang, Z. Shen, Biosens. Bioelectron. 17 (2002) 541.
- [151] Q. Wang, W.-L. Song, L.-Z. Fan, Y. Song, J. Membr. Sci. 486 (2015) 21.
- [152] T. Evans, J.-H. Lee, V. Bhat, S.-H. Lee, J. Power Sources 292 (2015) 1.
- [153] H. Xue, Z. Shen, Ch Li, Biosens. Bioelectron. 20 (2005) 2330.
- [154] B.W. Howlett, The Fabrication & Properties of Carbon Fiber/Metal Matrix Composites, Plastic Institute Conference on Carbon Fibers, 1991.
- [155] M.S. Annette, M. Renate, Perspectives for the mechanical manipulation of hybrid hydrogels, J. Poly. Chem. 2 (18) (2011), https://doi.org/10.1039/c0py00129e. www.rsc.org/polymers.
- [156] W. Ke, W. Jingshen, Y. Lin, Z. Hanmin, Mechanical properties and toughening mechanisms of polypropylene/barium sulfate composites, J. Comput. Part A: Appl. Sci. and Manu. 34 (2003) 1199–1205.
- [157] A. Lustiger, C.N. Marzinsky, R.R. Mueller, Spherulite boundary strengthening concept for toughening polypropylene, J. Polym. Sci. Part B: Polymer Physics 36 12 (1998).
- [158] B.I. Chaudhary, R.P. Barry, M.H. Tusim, Foams made from blends of ethylenestyrene interpolymers with polyethylene, polypropylene and polystyrene, J. Cell. Plast. 36 (397) (2000), https://doi.org/10.1106/3YH7-YK2C-XPVM-TYNK.
- [159] T. Weihua, T. Jian, Y. Huilin, J. Riguang. The compatibilization effect of ethylene/ styrene interpolymer on polystyrene/polyethylene blends, J. Polym. Sci. Part B: Poly. Phy. 45 (16) (2007).
- [160] T. Jian, T. Weihua, Y. Huilin, J. Riguang. Mechanical behaviors of ethylene/ styrene interpolymer compatibilized polystyrene/polyethylene blends, J. Appl. Polym. Sci. 104 (6) (2007).
- [161] A. Hiltner, H.Y. Chen, S.P. Chum, E. Baer, Phase behavior of partially miscible ethylene-styrene copolymer blends, J. Macro. 34 (2001) 4033–4042.