

Review Article

A Review of Some Significant Advances in Nano Fibrous Composites

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The article reviews some significant trends in development of nano fibrous composites. Polymeric nanofibers as one of the most known nanotechnology products have huge potential applications in many fields due to their high aspect ratio and porosity, being capable of formation of three-dimensional structures and having great mechanical and biological properties. Chitosan is a natural abundant polymer which has attracted huge interests in biomedical and biological industries due to its biocompatible, biodegradable, and non-toxicity properties. Electrospun polyurethane nano fibres with needle punched recycled non wovens from polyester textile wastes and bottles have been combined into composite structures having different stacking sequences and intended as an innovative sound absorption material so as to address the problems related to noise pollution and waste generation.

Keywords: Nanofibres; Chitosan; Composite; Sound absorption; Nonwoven; PET**Introduction**

Due to its simplicity and economy the electro spinning holds promise as a method of producing a variety of polymeric fibres as micro and nanometer scale fibres. In this method a high voltage source has been used to inject charge having a specific polarity, into a polymer solution or melt, that is subsequently accelerated toward a receiver that has opposite polarity [1,2]. The charges in the polymer jet carry the polymer in which the charge is embedded in the direction of the electric field. This is the mechanism that moves charge from the reservoir of liquid polymer to the collector, and thereby completes an electrical circuit which provides the energy needed to accelerate the polymer, to increase its surface area, and to drive the flow and deformation processes which change the shape of the liquid into a jet [3,4].

Mankind has caused waste generation [5]. During past decades, a great deal of waste has been generated owing to the increase in textile consumption. One option has been to use these wastes in low value added products and another option has been to just discard them [6]. New areas of use must be found in order to achieve environmental, economic, and sustainable gains and protect future generations [7,8]. Manufacturing nonwovens from textile wastes for various industrial purposes is one of the recycling methods.

Chitosan-Gelatin-Montmorillonite Nanocomposite Nanofibers

Electrospun nanofibers possess special characteristics, such as large surface to volume ratio, high density of pores, and excellent surface adhesion, and find broad areas of applications. Of the polymers used in electro spinning, nanofibers from biocompatible polymers have shown promise in uses in biomedicine, including wound dressings, drug delivery, tissue engineering scaffolds, etc [9-12]. The unique properties of nanofibers, such as high surface to volume ratio, small

pore size, high oxygen-permeable porosity, and ease of fabrication made them such practical materials [13-17]. Chitosan is a functional linear polysaccharide, derived from the deacetylation of chitin, which is the second most abundant biodegradable natural copolymer consisting of 2-amino-2-deoxy-D-glucose and 2-acetamido-2-deoxy-D-glucose units linked with b-(1-4) bonds [18]. The content of free amino groups in polysaccharide, defined as the Degree of Deacetylation (DD), can be used to differentiate between chitin and chitosan [19]. Chitosan has been gaining increasing importance in the biomedical field such as tissue engineering and wound dressing owing to its good biocompatibility, biodegradability, and low toxicity. It also contains free amino groups which makes it a positively charged polyelectrolyte in pH below 2-6. However, this property makes chitosan solutions highly viscous complicating its electrospinnability [20]. To overcome chitosan electrospinnability challenges, polymer blending is suggested more specifically with a polyelectrolyte for its ability to be negatively charged due to pH conditions [21-23]. Hence, gelatin (gel), denatured derivative of collagen can be used as second component. Collagen molecules are mainly stabilized by intra and inter-chain hydrogen bonding [24]. When collagen is heated above its denaturation temperature, hydrogen bonds that stabilize the adjacent polypeptide chains are destroyed. Individual a-chains and b-chains are produced from the intact trimers (c-chains) and thus the rigid triple helical collagen state is transformed into a single-stranded, random-coil state (helix-coil transition) resulting in the production of gelatin [25]. Because of its biodegradability, biocompatibility, and non-immunogenicity, gelatin has been widely evaluated as a prostheses, tissue scaffolds, and incorporation into drug delivery systems and wound healing materials [26]. Several researches on electrospinning of gelatin and chitosan blend nanofibers indicate that both chitosan and gelatin possess good biocompatibility, biodegradability, and commercial availability [27-30]. However, use of conventional cross-linking agents such as glutaraldehyde which

can lead to toxic side effects, may impair the biocompatibility of cross-linked blend nanofibers [31]. Solving this problem, layered silicates may substitute the toxic chemical cross-linking agents and act as physical cross-linking in gelatin and chitosan. Montmorillonite (MMT) has been attracting great attention due to its remarkable improvement in mechanical, thermal, flame-retardant, and barrier properties of polymeric composites with small amounts (1-10wt %) of MMT fillers added. These property improvements are attributed to the nanometric thickness and high aspect ratio of the individual clay platelets, as well as to the nanocomposite morphology with the platelets being exfoliated and well-dispersed. Also, due to silicate nature of MMT, it can be a great candidate to produce bone tissue scaffold in case of being used in biomaterial base nanofibers. Previously, gelatin/MMT-chitosan nanocomposite scaffold has been developed by the freeze-drying method using ice particles as porogen materials [32]. Also, gelatin-chitosan/MMT microspheres have been prepared by emulsion/chemical cross linking technique for drug delivery applications [33]. However, specific study on the electrospinning of gelatin-chitosan-MMT nanofibers has not been reported yet. In this research, chitosan-gelatin/MMT blend nanofibers were electrospun to investigate the possibility and changes in nanofiber formation. Hence, understanding the behavior of such nanofibers in this new process is utmost significant and this work examines the morphology and miscibility of nanofibers using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectrometer/Attenuated Total Reflectance (FTIR/ATR), and X-Ray Diffraction (XRD) techniques.

Acetic acid has been used as solvent in the electro spinning of Gelatin-chitosan/MMT nanocomposite nanofibers. The electrospinnability of chitosan nanofibers is enhanced by Gelatin. Further, as MMT acts as compatibilizer, introduction of MMT in gelatin-chitosan blend tends to enhance electrospinnability of resulted nanocomposite nanofibers [34]. The morphology of nanofibers was investigated using SEM. The miscibility and interaction of gelatin and chitosan and MMT was tested using FTIR/ATR. XRD result confirms the exfoliation of silicate layers in gelatin-chitosan matrix. The resulted nanofibers can be great candidate in biomedical application especially when bone tissue scaffold is needed.

Nanofibrous Composite from Recycled Nonwoven

An ecological option for sound absorption in the automotive industry is the use of recycled conventional nonwovens [35]. The health and comfort of mankind is adversely affected by noise [36]. Hence it becomes important to decrease the undesirable noise in the environments. Textile sound absorbers have increasingly been used in noise reduction [37]. Hard and smooth surfaces reflect most of the incoming energy while soft and porous surfaces such as fabrics absorb most of it [38]. Needled recycled nonwovens which are used in drainage, filtering, separation, soil protection and partly erosion control are good sound absorbers due to their three-dimensional, complex and multi-fiber structure [39].

The sound energy can be transformed into thermal energy by the principle of the sound absorption theory [40]. Although there are plenty of factors affecting sound absorption such as thickness, density, open-cell percentage, velocity of the air particles, porosity, compression, fiber size it is not easy to find a direct simple relation

between the Sound Absorption Coefficient (SAC) and these factors [41-43]. Two methods are used for measuring the acoustical properties of the textile fabrics; impedance tube method and acoustical chamber method. Hearing range for human ear is 0-20,000 Hz [44]. SACs differ according to the frequency applied. SAC value is rated between 0 and 1. A SAC value of 0.5 is critical in order to evaluate the efficiency of an absorber [41]. Nanofibers have gained great attention as sound absorbing materials [45]. They could act as acoustic resonant membranes and dampen the sound [46]. Nanofibers have larger surface area to volume, very small pore size and high porosity level when compared to conventional fibers [47,48]. Electro spinning is the most widely used, efficient and simple nanofiber manufacturing method [47,49]. Porous structure of nanofibers leads sound waves to have high interactions between the molecules [50]. Traditional sound absorbing materials are good at high frequency range (>2500 Hz) while they are not so good at low (0-500 Hz) and medium frequency ranges (500-2500 Hz) [51,49]. Nanofiber enhanced absorbers have the potential of increasing SAC values for low and medium frequencies due to high surface area and friction in the pores without any thickness or weight disadvantage [52]. Traditional insulation materials such as glass wool, mineral wool, rock wool and polystyrene have some side effects for both human health and the environment during production and usage [53]. Mineral fibers may induce skin irritation and lay down in the lungs and cause health problems when inhaled [54]. Researchers studied with nanofibrous materials with various polymers such as Polyacrylonitrile (PAN), Polyurethane (PU), Polyamide (PA), Polyvinyl Alcohol (PVA), Polystyrene (PS), Polyvinyl Chloride (PVC), Polyvinylpyrrolidone (PVP) [55-59]. PU and PAN nanofibers have been produced and various nanocomposite structures have been prepared and investigated for the relation between the areal density of the nanofiber layers and the SACs [60]. The SACs became higher than 0.6 around 1500-6000 Hz frequency range by adding nanofibers. Decreases have been examined in SACs as the weight of the nanofibers were increased to 3g/m² and after displaying a minimum value at 3g/m², the SACs started to increase by the increment of the weight to 5g/m². 10 and 17g/m² PAN nanofibers have been produced and some spacer fabrics reinforced with the nanofibers and investigated the effects of nanofiber layer number and nanofiber weight on SACs [61]. They declared that number of the nanofiber layers have more effect on sound absorption than the weight of the layers. However, weight of the nanolayers has been expressed and is more important than the number. The reasons for these controversial results may be that the materials are different SACs increase as the nanofiber weight increases until a critical point. Also the effects of nanofiber layer number and weight on sound transmission loss have been compared. It has been reported that the number of layers is more important than the weight. PVP, PS, PVC and mixture nanofibers have been produced by needle electrospinning and studied for the effect of nanoweb thickness on SAC [62]. The SAC value obtained with the 2.52 cm thick PS/PVC mixture was 0.98/0.99 at 2000-6000 Hz frequency range. A nanoweb has been obtained with an areal density of 30g/m² and an average diameter of 800nm from PA and compared SACs of multilayer nanofiber surfaces with the same weight microfiber fabrics and reported that the SACs of both the microfiber fabrics and the multilayer nanoweb were the same until the frequency range of 1600Hz with a maximum value of 0.09 [63]. The reason for such low values may be that produced fibers were

close to micro scale (800nm). SACs of the multilayer nanowebs were higher than the microfibers at 1600-4000 Hz frequency range with maximum value of 0.45 at 4000Hz where the maximum SAC value for the microfibers were 0.30. Researchers studied the effects of nanoweb layer number, nanoweb weight and polymer type on SAC values in nanofiber enhanced materials and reported that nanofiber enhanced materials have the potential of being used as sound absorbers. Although there are numerous other studies in literature concerning sound absorption properties, to the best of authors' knowledge, nanofiber enhanced recycled PET nonwovens with different layering was studied for the first time. This study shows that the low value-added recycled nonwovens were up cycled to higher value-added sound absorbing composites by the incorporation of nanofibers. The main aim was to obtain light and efficient sound absorbing materials. Produced composite materials have the potential of replacing pretty much thicker and harmful sound absorbing materials in the market.

The production of new sound absorbing nanofibrous composites were executed and results indicated very good improvement on SAC values [64]. The most remarkable outcomes and distinctions of the study may be summarized as follows:

a) H250 nonwovens have shown considerable SAC increase in the presence of nanowebs 1520 and 1320 in all frequency ranges. But, nanowebs have shown a significant increase on A250 nonwovens for only low and medium frequencies. The reason is that H250 nonwovens have lower SACs for all frequencies and so do their NRCs. A250 is in fact a good sound absorber and it is much more improved by the addition of nanowebs. However sandwich structures were not drastically improved at high frequency ranges.

b) A250-1320-A250 has been considered as the most ideal sample produced in this study with the highest NRC, (NRC $\frac{1}{4}$ 0.504, thickness $\frac{1}{4}$ 3.24mm).

c) An excellent improvement on sound absorption could be achieved by reinforcing the nonwovens with nanofibers. When compared to commercially available sound absorbing materials having at least 2 cm thickness, the nanofiber added nonwovens are promising good sound absorption without the weight penalty.

d) When the two nanowebs produced for 20 min were compared, it was seen that the resultant finer fibers (296.5 nm) made a better improvement both in SACs and NRCs than the others (509.9nm).

e) The low value-added recycled textiles which are generally used in geo textiles will find a different usage and could be transformed into high-value acoustic products.

Conclusion

Chitosan is a natural abundant polymer which has attracted huge interests in biomedical and biological industries due to its biocompatible, biodegradable, and non-toxicity properties. However, electrospinning of chitosan is found to be a great challenge, blending it with other polymers such as gelatin was explored as means to improve the morphological deficiencies of chitosan nanofibers and facilitate its electrospinnability. On the other hand, Montmorillonite (MMT) has been attracted great attention due to its remarkable improvement in properties of polymeric composites nanofibers. The main objective of

this work was on effect of concretion of gelatin-chitosan blends and MMT on morphology of resulted Nanocomposite nanofibers. The x-ray diffraction data demonstrated the exfoliation of MMT layers. The morphology of electrospun chitosan-gelatin-MMT composite nanofibers was characterized using Scanning Electron Microscope (SEM). The miscibility of blend was determined using SEM and Fourier transform infrared spectrometer/attenuated total reflectance.

PU solutions of 12, 13, 14 and 15 wt % concentrations were prepared for nanofiber optimization studies. Scanning Electron Microscope (SEM) images showed that the bead free nanofibers were obtained with diameters 296.5 and 509.9 nm from 13 and 15 wt % PU concentrations, respectively. In order to evaluate the potential of nanofibers and nanofiber-recycled nonwoven composites as noise reduction materials; sound absorption coefficients (SACs) were measured and noise reduction coefficients (NRCs) were calculated. The most ideal sample was regarded as the 3.24 mm thick sandwich structure (recycled nonwoven-nanofiber-recycled nonwoven), coded with A250-1320A250 with a 0.504 NRC value. When the two nanofiber diameters were compared, finer nanofibers (296.5nm) and finer nanofiber enhanced nonwovens had better NRCs than the thickers (509.9nm) of the same. The developed composite materials can be regarded as promising sound absorbers.

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