PERFORMANCE OF POLYVINYLIDENE FLUORIDE–CARBON NANOTUBES COMPOSITE

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Abstract: The Polyvinylidene Fluoride polymer it is unique materiel, which drown huge amount of attention in nowadays. Even though it has been known since 1969 year and many aspects of the polymer have been studied good enough, there are still much more that need to be studied further, because the Polyvinylidene Fluoride still did not yet reveal his full potential. The strongest side of Polyvinylidene Fluoride is the biggest piezoelectronic respond among all commercially available polymers. Polyvinylidene Fluoride is prepared in various forms: thin films, bulk samples, fibers. PVDF fibers attract the most attention because of high flexibility, lightweight, mechanical stability, chemical inertness.

Keywords: Polymer, carbon nanomaterial, phase composition

1 INTRODUCTION

Polyvinylidene Fluoride (PVDF) is a semicrystalline, non–reactive Thermoplastic that is approximately fifty presents amorphous. The Percentage of crystallinity is based on the Chain ordering defects. PVDF is a Plastic material belongs to fluoropolymer family [1].

Polyvinylidene Fluoride (PVDF) is a semi–crystalline, high purity thermoplastic fluoropolymer. PVDF is readily melt–processible and can be fabricated into parts by injection and compression molding [2].

Thanks to its excellent combination of properties and processability, PVDF has become the largest volume of fluoropolymers after PTFE.

PVDF is available commercially in a wide range of melt flow rates and with various additives to enhance processing or end use properties.

The atomic structure of PVDF is represented by monomer −CH2CF2−. The molecular weight of the monomer is between 16 and 17 kg/mol. The monomer −CH2CF2− has strong electrical dipole moment with regards to electronegativity of fluorine atoms. The monomer forms chains with perpendicular orientation of dipole moments. The PVDF’s properties, as with most polymers, has been intensively studied. The main focus of research has been done on two most important aspects, the thirst is polymorphism and second is piezoelectronic respond [2].

The polymer has many electronic applications, especially as jacketing materials for plenum–rated cable used in voice and video devices and alarm systems. The low flame spread and smoke generation of PVDF is a prime asset in these applications.

Emerging applications of PVDF include fuel cell membranes, and components for aircraft.

2 MATERIALS

2.1 POLYVINYLIDENE FLUORIDE

PVDF is semicrystalline material crystallized into five different crystal phases: α, β, γ, δ, ε obtained by different process parameters [1].

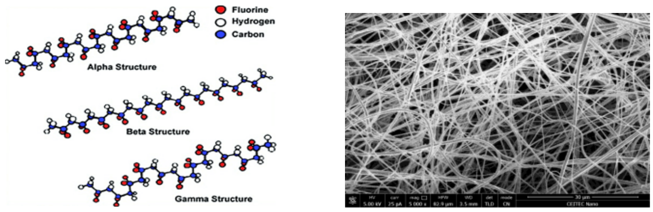


Figure 1: Common phases of PVDF [4], SEM image of PVDF

The most stable at room temperature α phase is commonly synthesized among other phases, although the α phase is electrically neutral (non−polar), because of its antiparallel dipoles' alignment [1].

After applying mechanical stretching of alignment, high pressure, changing temperature of crystallization of melt the α phase can be transferred into oriented β phase [2]. The β phase is the most important due to its superior electrical, ferro−electrical and pyro−electrical properties in compare to other phases. Has been found the β phase not only represents huge potential due to the strongest piezoelectric respond among all PVDF's phases, but also the PVDF itself has the strongest piezoelectric response amongst all commercial polymers.

PVDF represents extraordinary mechanicals and chemical parameters such as:

Deformation resistance, absorption resistance, chemically resistant, stability to radiation, high working temperature (from –49° to 302° F), electrical insulator, radiation stability, high Curie point (217.4° F), high purity.

Such combination of properties makes PVDF useful for varieties of application where the polymer is used in:

Aerospace, biosensors, biotechnologies, pharmaceutical, microelectronics, pressure sensors, insulator for batteries.

Well−characterized properties make the PVDF leader of piezoelectric polymers.

2.2 CARBON NANOTUBES

Carbon nanotubes are unique carbon fibers with similar structure of fullerene. As other unique properties have been discovered such as remarkable mechanical and electronic properties unique Roman spectra, thermal conductivity, toughness, interest to nanotubes started to grow and their potential use in wide varieties of applications especially in nano–dimension electronics and medicine [3].

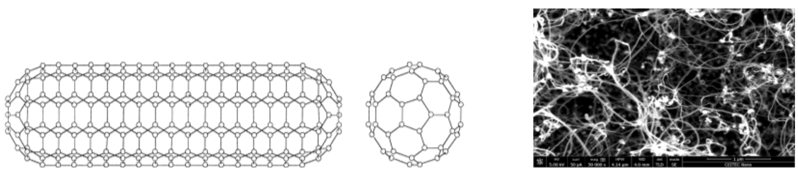


Figure 2: Structure of nanotube [3], produced nanotubes

The structurer of carbon nanotubes is similar to structure of 3D graphite and memorize honey camp. An ideal nanotube represents hexagonal network of carbon atoms rolled up to form seamless cylinder. These cylinders are represented by layers of fullerene molecules. Base on amount these layers, nanotubes are subdivided on two types: single−walled nanotubes (SWNT) and multi−wall nanotubes (MWNT) [3].

3 ELECTROSPINNING OF PVDF FIBERS

There are many available commercial technologies of producing Nanofibers, however there is one technology which allow produce fine fibers [4].

Electrospinning is unique self–assembly technology offers wide variety of adjustable parameters to produce required fibers. Electrospinning is the thirst technology allowed to produce fibers which formation is given by electrostatic forces rather mechanical. Fibers obtained by using electrospinning are self–organizable [5]. Thanks to rather not completable basic setup, producing huge range of nanofibers and controlling their morphology by changing process parameters the electrospinning gained huge popularity and widely used in nowadays [4].

Parameter	Increasing	Decreasing	Orientation	Morphology	Quality
Working Distance (WD)	There is strong possibility fibers will not be collected on counter electrode.	With decreasing WD the solvent in precursor will not dry out completely, thus thickened drops of precursor will accrue, furthermore fibers will not be properly formed.	With decreasing working distance.	It appears, that with decreasing of WD, still wet precursor collects even more fibers around itself which leads to creation thickened clusters of fibers.	Thickened drops defect that appears at small WD can significantly lower piezoelectronic and triboelectric effect due to its electroneutrality.
Voltage	High voltage causes stretching of Taylor cone by higher generated charge which leads to faster formation of fibers from smaller amount of precursor [6].	Lover voltage shrinks Taylor cone, thus bigger amount of precursor can easily degrade on the top of needle and compromise entire process by clogging of needle [6].	Does not change	With increasing voltage produces fibers become thinner. In case of successful formation [6].	Both thick and thin fibers are used in different applications.
Number of rotations	By increasing numbers of rotation counter electrode more fibers are produced.	With lower number of rotations less fibers are produced.	High number of rotations allowed to produce oriented (parallel) fiber; chaotically orientated fibers are produces by lower number of rotations.	The morphology of parallel and chaotically fibers is pretty much same.	In some cases, with high number of rotations, produced fibers have tendention to create areas with nonhomogeneous thickness of produced fibers, although fibers produced by lower number of rotations have homogeneous thickness.
Needle diameter	It has been proved needles with smaller diameter clogging less often rather with bigger one. By using Scanning Electron Microscopy has been proven, fibers produced by using needles with smaller diameter have tiniest diameters and vice versa. However, in different cases has been found no correlation of fibers and needle diameters [7].				

Table 1: Summarization of processing conditions on produced fibers

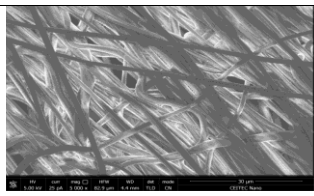
Sample	Parameters	D33 (µC/N)	SEM image
29–1,2	Precursor: PVDF 20% 275 WD: 20 cm Doses: 40–50µl/min Voltage: 50kV Humidity: 30->20% Rotations: 2000 min^{-1} Hot air mode: On	≈ 20	

Table 2: Characterization table of produced samples

4 THESIS PERSPECTIVES

The main object of the semestral/diploma thesis is based on comparing properties of pure PVDF material with PVDF–CNT composite. The most important aspect of the entire thesis is producing pure PVDF material using technology calls electrospinning. Once material is produced it needs to be evaluated base on piezoelectronic respond. Since PVDF has the strongest respond among all polymers, piezoelectronic respond resp. measurement of d33 parameter is the easiest way to prove functionality of produced material. Parameters of material with the strongest respond will be used to produce composite based on pure PVDF material and Carbon nanotubes. By comparing pure PVDF and PVDF–CNT composite we will be able to prove whether or not Nanotubes has any effect on properties of PVDF.

The table 1 represents parameters which effect the produced material. The effect of singe parameter has been defined experimentally. To determent if there are any changes in Morphology of the produced material the morphology has been studied using Scanning electron Microscopy (SEM). It has been proven number of rotations effect orientation.

The second table contains summary of parameters of the best sample. These parameters will be used to produce PVDF–CNT composite. Unfortunately, the situation around coronavirus makes further progress problematic.

The technology calls Focused Ion Beam (FIB) will provide more detail information regarding cross–section of single fibers. It has been found that certain samples produce by same parameters has sings of hollows inside of fibers which give us a ground to try to produce coaxial fibers using CNT. However, there are still unknowns and speculations about mechanism of their formation which require further studding and running more experiments.

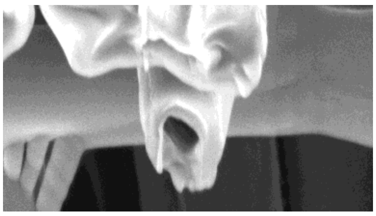


Figure 3: Hollows inside a fiber

5 ACNOWLEDGMENTS

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6 CONCLUSION

Polyvinylidene fluoride one of important polymer with huge scientific interests. PVDF is represented in five crystalline phases: α, β, γ, δ and ε. Besides having the strongest piezo- respond of β phase, it also combines pyro-and ferroelectric properties, which is important in many applications. The material has found his place in many areas we all familiar with such as solar panels, batteries, alarm systems, medical masks, filters etc. however, the material has more to offer to all aspects of applied science, manufacture, and medicine.

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