Use of Electrospinning to Improve the Dispersion of Inorganic Nanofillers in Silicone Rubber

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***Abstract*— Electrospinning is a simple and easy process to produce nano-sized fibers from electrostatically driven jet of polymers. In this paper, electrospinning has been used to disperse inorganic nanofillers into silicone rubber matrix to produce silicone nanofibers (or nanodroplets). These nanofibers will encapsulate the fillers. Common inorganic nanofillers for outdoor insulation, such as nano fumed silica (with a diameter of ~7 nm) and nano natural silica (with a diameter of ~10nm) are used and electrospun with silicone rubber to enhance its dielectric properties. Samples with 3% nanofillers were prepared separately by using a high shear force mixer and by using the electrospinning setup. The dispersion of nanofillers was characterized and compared by means of scanning electron microscopy (SEM). The thermal gravimetric analysis (TGA) was also used to analyze the thermal degradation of nanofilled silicone rubber.**

I. INTRODUCTION

There is a strong trend towards the development of polymer nanocomposites during the last few years. The large specific area between nanofillers and polymers leads to substantial improvements in properties of nanocomposites. It has been reported that the use of nanoparticles in the matrix of polymeric materials can greatly improve the thermal, mechanical and electrical properties of polymeric composites and reduce cost [1-3].

The properties of nanocomposites are highly dependent on how well the particles are dispersed within the polymer matrix. Achieving a uniform dispersion of particles is difficult as the high surface energy of nanoparticles makes them very easily agglomerate. There are several mixing methods like conventional mechanical mixing, ultrasonic mixing, and mixing after chemical surface modification of particles. Among these methods, the most effective way is by using the particle surface modification. Although a high shear force mixer can give a good dispersion for large nanoparticles or micron-particles but for fillers with the sizes in the range of several to hundred nanometers, it is not efficient. Since interfacial forces between particles become much stronger, the conventional mixing facilities with their intrinsic limitations cannot break apart the agglomerates [4]. Surface modification of nanoparticles decreases the surface energy between nanofillers resulting in more particle separation and thus a good dispersion of fillers within the polymer matrix. However, a specific type of surface treatment may work for one kind of filler, and not with some other filler. Further, excess use of chemical agents may result in inferior material properties.

Electrospinning (ES) is a well-known method which can produce fibers with diameters ranging from submicron diameter to nanometer diameter, with controllable lengths [5]. ES method uses electrostatic forces to stretch the charged jet of polymer solution causing a tiny stream of solution to eject from the high voltage spinneret. When the jet flies away from the high voltage tip towards the grounded collector, it bends into a complex path and becomes further stretched and thinned in the large ratios. A proper solvent should be used to prepare the polymer solutions for ES. During the above process the solvent will evaporate and eventually solid fibers are left on the collector. Under a sufficient feeding of solution, the nanofibers will be continuously fabricated. ES has been successfully used to produce nanofibers encapsulating nanoparticles [6-7].

Polymer solutions like, polyethylene oxide, polyvinyl chloride, and polyamide have been successfully electrospun. On the other, polymers like silicone rubber that are good insulating materials with low viscosity, low conductivity and low molecular weight are difficult to electro spin. In this paper, by making suitable changes to the existing ES technique, the ES method is demonstrated to improve particle dispersion in RTV 615 silicone rubber. Nano fumed silica (NFS, average particle size of 7nm) and nano natural silica (NNS, average particle size of 10nm) were used as fillers to reinforce two-part silicone rubber RTV 615.

II. EXPERIMENTAL

A. Sample preparation

The viscosity and conductivity of polymer solution will influence the formation of nanofibers [8]. Therefore, pure low viscosity and low conductivity silicone rubber cannot electrospin. Although silicone rubber is hydrophobic, it is compatible with alcohol; hence, ethanol was used as a solvent. The presence of ethanol can increase the conductivity of silicone rubber solution for the purpose of spinning as ethanol easily evaporates during the process. In addition, the viscosity of polymer solution also increased after mixing. Both these characteristics help ES. As the volume of ethanol affects the ES work, it should be well controlled. From the experiments the optimized volume of ethanol should be around half that of the silicone rubber resulting in a good ES silicone rubber solution. It should be mentioned that after mixing the color of silicone rubber solution was changed from transparent to white. Fig. 1 shows the schematic diagram of the ES set up. For ES part, only the mixture of RTV615 part A, nanofillers and ethanol was electrospun. The polymer solution was delivered to the spinneret at a constant flow rate which was controlled by a pump. The applied high DC voltage is kept between 10-20kV and the distance between the spinneret and the ground collector is set between 10 and 30cm. Actual distance and voltage levels were adjusted based on the polymer solution.

Part B, curing agent, was added into the collected electrospun polymer to cure the composite. The final mixture was degassed in a vacuum oven, and then poured into moulds. RTV615 silicone rubber will cure sufficiently in 24 h at 25 ℃ to permit handling. Thus the samples were cured in room temperature for 24 h and post-cured at 87℃ in the oven for 4 hours to achieve optimum properties.

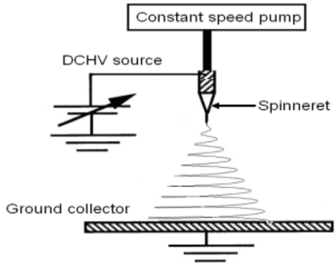


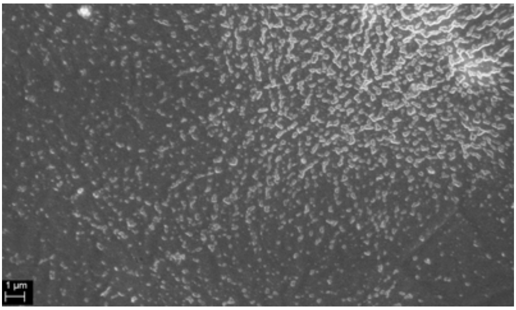
Fig. 1. Schematic diagram of electrospinning process.

In order to compare the improvement of particle dispersion, a high shear force Ross laboratory mixer (model HSM-100LSK) was used to make the samples containing the same percent of nanofillers by weight as those samples produced using ES.

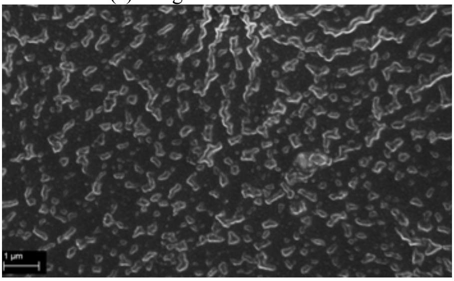
III. RESULTS AND DISCUSSION

A. SEM analysis

It has been reported that a charged jet of a low molecular weight polymer solution will form droplets due to electrospraying, as opposed to electrospinning [9]. If the fibers or droplets are still in nano size both electrospinning and electrospraying will not affect the particle dispersion. In order to check whether it is electrospinning or electrospraying, RTV615 part B was mixed into silicone rubber solution before electrospinning. To accelerate curing, the collector plate was heated up to 200 ℃ during the electrospinning process. The collected polymer was checked under SEM which is shown in Fig. 2.



(a) Magnification is 10K

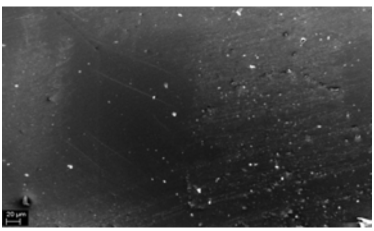


(b) Magnification is 21.26K

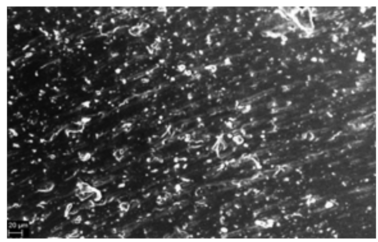
Fig. 2. SEM images of quickly cured silicone rubber during electrospinning process.

From Fig. 2, it is clear that some of the collected compounds are droplets and some of them look like fiber segment. However, the sizes of these droplets/segments were all in the nanometer diameter and most of them were uniformly distributed. It is therefore assumed that the fillers contained in these volumes should be also in nano sizes.

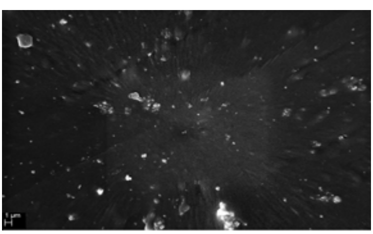
Fig. 3 shows the cross section morphology of samples which contained 3% of NFS and NNS by weight and prepared by using high shear force mixer and ES. Because of the cutting problem there are some striations and flakes on the surfaces of samples. Although, all of the samples contained 3% of fillers by weight, electrospun samples obviously showed more uniform particle distribution than those of high shear force mixed samples. Most of the particles in electrospun samples have sizes below 500nm while in high shear force mixed samples there were large agglomerations in the range of several mi-cron-meters. In addition, particle distribution is not uniformly distribute.



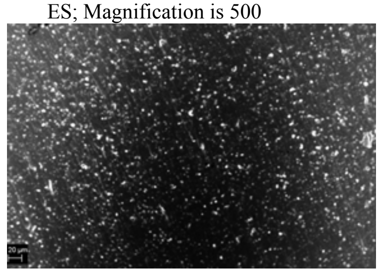
(a) Silicone rubber with 3% NFS prepared by high shear force mixer ;Magnification is 500



(b) Silicone rubber with 3% NFS prepared by ES; Magnification is 500



(c) Silicone rubber with 3% NNS prepared by high shear force mixer; Magnification is 5K

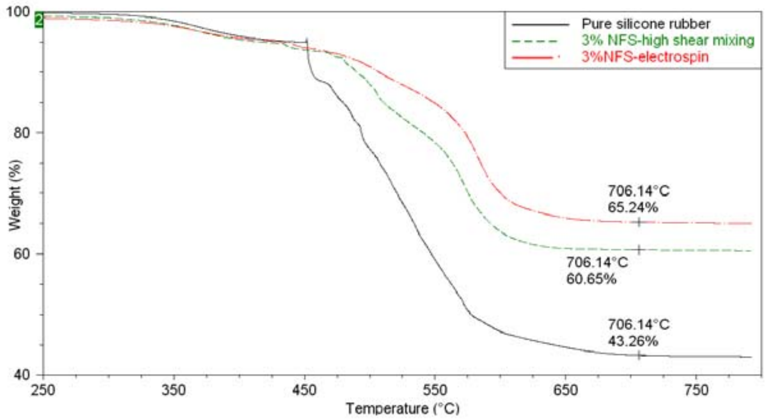


(d) Silicone rubber with 3% NNS prepared by ES; Magnification is 500

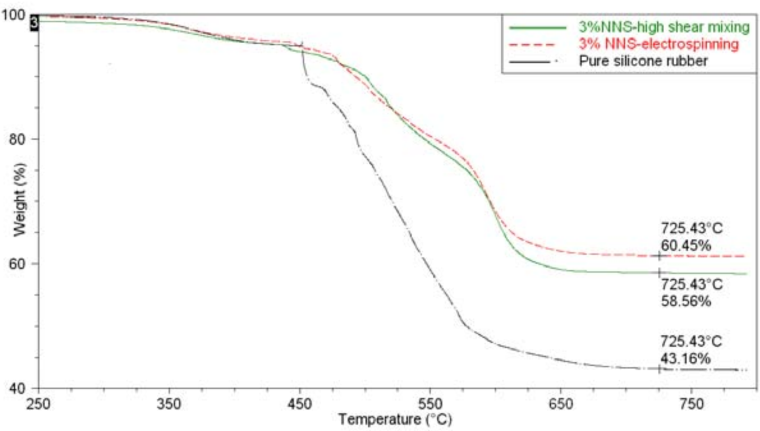
Fig. 3. SEM images of particle dispersion of samples with 3% fillers by weight.

B. Thermal gravimetric analysis

The thermal gravimetric analysis was conducted on silicone composites with 3% nano-fillers of both types (NFS and NNS) and pure silicone rubber without any filler. The measurements was done with a TA instrument TGA-Q500 which was operated in the atmosphere of air and the temperature increased at a rate of 20℃/min from 250 ℃ to 800 ℃. The results are shown in Fig. 4. It can be seen that the samples with nanofillers have higher residual weight in TGA curves than pure silicone rubber. Further, electrospun samples have higher residual weight than high shear force mixed samples. The fillers helped decreasing the speeds of depolymerization of pure silicone rubber which was obtained from the lower curve slopes of nanofilled samples. However, it seems that electrospun NFS sample has a better thermal stability than electrospun NNS samples.



(a) Silicone rubber with 3% NFS



(b) Silicone rubber with 3% NNS

Fig. 4: Thermal degradation of samples with 3% fillers by weight and pure silicone rubber

Based on the SEM and TGA results, it can be stated that composites prepared using ES method have a better particle dispersion and thermal stability than those composites prepared using high shear force mixing method, for RTV615 silicon rubber. Also, use of ES method to disperse nanoparticles in low viscosity silicone rubber helps to eliminate chemical agents to surface treat the particles. The only additive used, ethanol evaporated during the electrospinning process; thus the samples will have fewer side effects due to added chemicals.

IV. Acknowledgements

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