

Mass Production of Nano-Composites Using Electrospinning

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Abstract — Many conventional polymer processing technologies for compounding micro/nano composites are known in the art. These methods include direct use of high shear mixers, roll mixers, Banbury mixers, and extruders. With recent interest in advanced composites with nanoscale fillers, efforts have been made to enhance conventional processing technologies as the imposed input energy is often ineffective at breaching the energy barrier to breakup agglomerated nano-filler structures. Drawing on inspiration from the fiber spinning industry, it is presented here that, fundamental principles for extensional flow deformation of a fiber-shaped polymer can be borrowed from emerging fiber spinning technology, electrospinning, in order to implement highly effective dispersive mixing. In this article, authors discuss about a novel method developed to produce nanocomposites at mass scale using mechanical and electrical forces using a proprietary apparatus. A case study using silica nano particles and silicone rubber matrix has been presented to demonstrate the capability of the system of dispersing nano particles in highly viscous matrix materials.

I. INTRODUCTION

Polymer processing can be characterized by: (1) mixing, (2) blending of polymers, and (3) compounding [1]. Compounding is the act of incorporating additives such as filler particles into a polymer matrix. Mixing, blending, and compounding are inherently complex as these processes involve specialized machinery and know-how to exploit polymer rheology and the response of a polymer to imposed stresses in order to produce materials with desired properties. Specialized machinery for polymer processing employ a combination of two forms of mixing: (1) distributive (extensive) and (2) dispersive (intensive) mixing. Distributive mixing is the act of kneading or distributing properties of a polymer to make a homogeneous material (e.g., uniform temperature). Dispersive mixing is more complex as it involves the application of stress, often shear stress, to break up the domains of the dispersed phase (e.g., filler particles) embedded in the polymer matrix. It is often a difficult challenge to dispersively mix and break up very small filler particles in the range of micro and/or nano scale since they tend to agglomerate due to their surface energy arising from Van der Waals forces.

II. THEORY

Researchers have studied the energy of the mixing process in order to fundamentally understand the challenges associated with compounding micro and nano particles in polymer composites. When stress is imposed on a liquid polymer composite, it causes material to flow and deform. Therefore, the energy intensiveness of the mixing process is dependent on the mode of deformation, which arises in either (1) a shear or (2) an extensional (e.g., stretching) flow [1]. In

order to breach the surface energy barrier and break up agglomerated particles in a polymer, the flow-field must be efficient at generating an interfacial surface so that the imposed stress can infiltrate (e.g., locally attack) the agglomerations [1]. The relationship between required input energy (e.g., mixing energy) and the surface generation (e.g., interfacial growth) was examined by Utracki (2002) [1] and the results are shown in Fig. 1. These findings suggest that extensional flows are more effective for dispersive mixing for three reasons: (1) interfacial surface area generation is greater, therefore (2) less mixing energy is required, and (3) extensional flow fields have a higher rate of spatial separation between two material points than in shear flows [1]. The work of Grace (1982) [2] also supports the notion that extensional flow deformation is more effective than shear flow deformation for breaking up the dispersed-phase domains in a polymer matrix.

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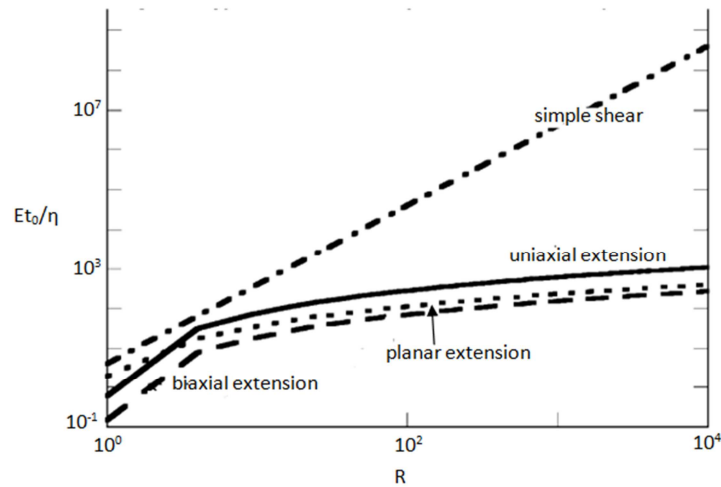


Fig. 1: Mixing energy (vertical axis) vs. interfacial growth (horizontal axis) for shear and extensional flows [1].

Investigations by Ristolainen et al. [3] and Demir et al. [4] have reported that the distribution of fillers in electrospun fibers is linked to how well dispersed the constituent phases are prior to electrospinning (e.g., pre-mixing). These investigations are based on mixing fillers in polymer by employing chemical methods such as in-situ emulsion polymerization, polymer

functionalization, and the reduction of metal salts into metallic nanoparticles. These are niche chemical methods and not universally applicable, and therefore suffer the same limitations as conventional methods previously mentioned. Electrospinning has also been pioneered by Jayaram's research group as a means of dispersively mixing fillers in liquid-phase fiber-shaped polymer (i.e., liquid ligaments) under the influence of an electric field. SEM images in the work of Bian et al. [5] revealed that fumed silica agglomerates are markedly smaller and fillers are distributed more uniformly in RTV 615 when dispersed with electrospinning in comparison to high shear mixing. Investigations in [5] focus on directly enhancing the dispersability of fillers in a polymer compound rather than investigating the dispersability of fillers in nanofibers as reported in [3] and [4]. However, existing electrospinning technologies suffer from major drawbacks including: low production rates, low filler loading, and pumping issues at high viscosity formulations limit the use of electrospinning for dispersion in mass production.

III. APPARATUS AND METHODS

Specifically, for the present apparatus named electrostatic disperser (see Fig. 2), filler particles are added to a polymer, the polymer-filled mixture is then deposited as a film on a rotating surface, and then the film is ejected from the rotating surface in the form of finger-like ligaments where they undergo extensional flow deformation. The ligaments are subjected to electrical forces induced due to the applied electric field between the rotating surface and a collecting surface, further contributing to extensional flow deformation and direct particle dispersion. In addition, it should be noted that the process is highly intensive as the composite is broken-down into hundreds of nanometer scale ligaments where particles are dispersed within each liquid ligament. Therefore, dispersion is performed simultaneously on all ligaments nearly at the molecular level rather than a bulk level like that of an extrusion process, resulting in better dispersion of micro/nano particles at higher loading levels and higher production rates relative to conventional methods. The electrostatic disperser can achieve production rates upwards of 60kg per hour. A case study using silica nano particles and silicone rubber matrix has been presented to demonstrate the capability of the system of dispersing nano particles in highly viscous matrix materials.

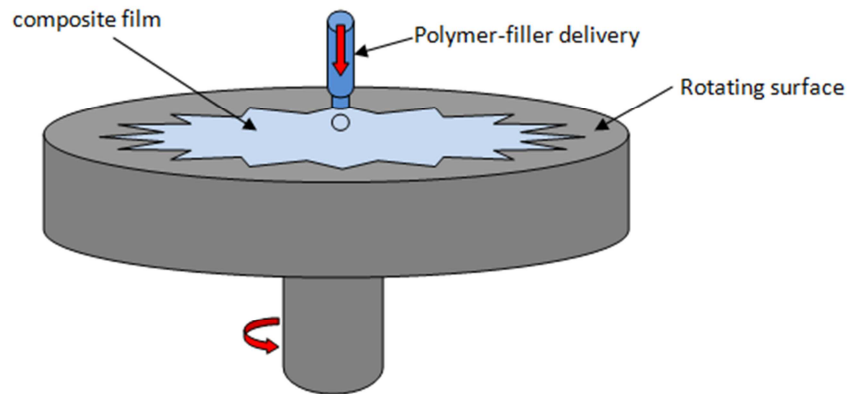


Fig. 2: Illustration of electrostatic disperser.

IV. RESULTS AND DISCUSSION

Polymer compounds with a highly aggregating filler, nano fumed silica (Aerosil® 300VS), in silicone elastomer (RTV 615) were prepared with conventional high shear mixing (Ross HSM-100LSK) and electrostatic disperser in order to examine the differences in filler dispersability between the two technologies. It is often very difficult to dispersively mix fumed silica nano fillers since they tend to heavily agglomerate due to their surface energy arising from Van der Waals forces, resulting in a marked increase in compound viscosity. As shown in Table 1, a maximum loading level of 10 wt. % was reached with high shear (Sample 2), while the further inclusion of fillers was restricted due to the very high compound viscosity. The addition of fillers transforms the compound into a gel-like high viscosity material and therefore, the viscosity was not measurable using a standard Malvern-Bohlin controlled stress/strain rheometer. Meanwhile, as shown in Table 1, loading levels upwards of 10 wt. % were prepared with electrostatic disperser (Samples 3 & 4) with a lower viscosity than that of the high shear mixed compounds at 10 wt. %. The reported findings substantiate that the reduced viscosity and tolerance for higher loading levels are linked to filler dispersion and distribution occurring at microscopic levels, enhancing the filler-polymer interaction.

Molecular weight (MW) measurements which were carried out from Gel Permeation Chromatography (GPC) before (Sample 1) and after (Sample 3) electrostatic dispersion are shown in Table 2. Polymer MW measurements after electrostatic dispersion were made by removing fillers from the compound according to standard GPC techniques. As shown in Table 2, since the polymer mass average molecular weight (Mw), number average molecular weight (Mn) and Polydispersity index (PDI) are nearly unchanged before and after electrostatic dispersion, the findings suggest that the polymer is not subjected to any process-related degradation, for example, chain scission or thermal degradation. In addition, transmission electron microscopy (TEM) images for composites with 10 wt. % fumed silica filler in RTV 615 are shown in Fig. 3 using the two mixing methods. These images further provide supporting evidence that the filler microstructure is severely aggregated for samples prepared with conventional high shear mixing than those prepared using electrostatic disperser. Fig. 4 shows a TEM image of pristine (in its original condition) fumed silica particles for comparison.

Table 1: Viscosity data of polymer compounds using different mixing methods.

Sample No.	Filler type	Filler concentration (wt. %)	Viscosity at a shear rate of $1s^{-1}$ (mPaS)	Mixing method
Sample 1	Fumed silica	0%	3550	-
Sample 2		10%	>1,000,000	Ross High Shear
Sample 3		15%	40,000	electrostatic disperser
Sample 4		21%	300,000	electrostatic disperser

Table 2: MW and Polydispersity index (PDI) before and after electrostatic dispersion.

Sample No.	Filler type	Filler wt. %	Average molecular weights (Da)		PDI (Mw/Mn)
			Mn	Mw	
Sample 1	fumed silica	0%	8,232	40,190	4.882
Sample 2		15%	8,364	41,636	4.978

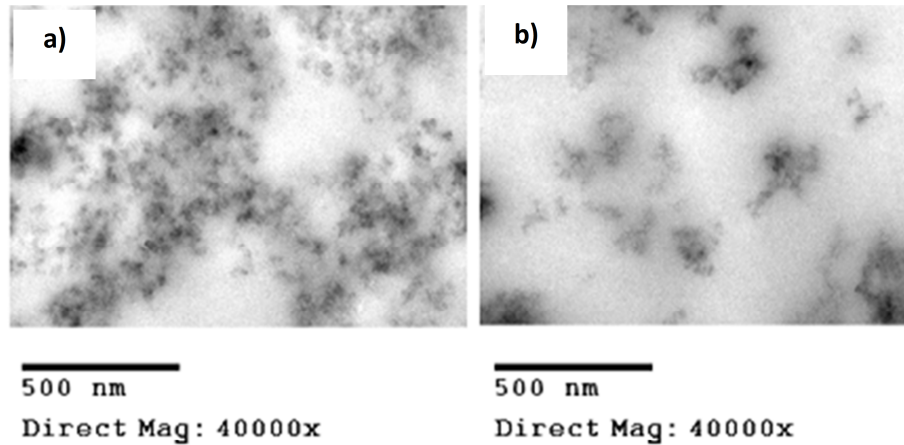


Fig. 3: TEM images of cured samples with 10% fumed silica in silicone. (a) high shear mixing, (b) electrostatic disperser

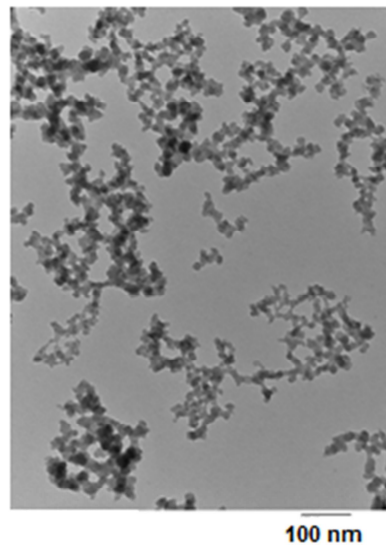


Fig. 4: TEM image of pristine fumed silica particles.

V. CONCLUSION

A novel mixing and dispersion apparatus named electrostatic disperser was developed based on fundamental principles of extensional flow deformation. A case study was carried out using

fumed silica nano particles and silicone elastomer to demonstrate the capability of the system of dispersing nano particles in highly viscous matrix materials such as silicone. The results revealed that the filler dispersion can significantly improve using the electrostatic disperser compared to conventional mixing technologies such as high shear mixing.

ACKNOWLEDGMENTS

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