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Research article

Dispersion of particulate in solvent cast magnetic thermoplastic polyurethane elastomer composites

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Abstract: Our research focuses on the processing of a thermoplastic magnetorheological elastomer (MRE) by solvent-casting a thermoplastic polyurethane (PU) elastomer with magnetic particulate for fused filament fabrication (FFF) applications. MREs are typically prepared by curing a thermoset silicone with magnetic particulate. Alternatively, thermoplastic MREs may be produced by the addition of magnetic particulate to a thermoplastic elastomer (TPE). FFF is a valuable manufacturing technique that allows for the creation of parts with inherent anisotropies. For the case of an MRE, FFF allows for the production of structures with tunable magnetic susceptibility along different axes. In these composites, the degree of particulate dispersion significantly affects the isotropy of material properties, which becomes increasingly important when small material volumes are used, such as in FFF. Incorporating solvent-casting as a method of producing polymer composites allows for greater control over the particulate addition method, leading to improved dispersion when compared to a polymer melt. For our purposes, composite films were produced in order to examine the effect of wet vs. dry addition of particulate on dispersion. The solvent used for casting was dimethylformamide (DMF). Preparation of polymer solutions included dissolution of PU in DMF to 20 w/v% followed by addition of the magnetic particulate. The particulates used were <150 μm iron powder and 2–4 μm magnetite powder. Composite solutions were made to concentrations of 20, 30, and 40 w/w% particulate to polymer by addition of either dry particulate or particulate pre-suspended in DMF. It was found that wet addition of particulate led to improvement in particulate agglomeration and magnetite particulate exhibited a significantly higher degree of agglomeration than iron.

Keywords: thermoplastic elastomer; magnetorheological elastomer; magnetic elastomer; solvent casting; particulate dispersion

1. Introduction

As the attention to magnetic soft materials has grown, magnetic thermoplastic elastomers (TPEs), also known as magnetorheological elastomers (MREs), have drawn people's interest on account of their potential for use in fused filament fabrication (FFF). MREs are composites consisting of magnetic particulate in an elastomeric matrix and possess mechanical properties that can be influenced by the presence of magnetic fields [1–3]. The ability to utilize these materials in FFF, commonly known as 3D printing, would allow for the easy and cheap manufacturing of soft actuators. Furthermore, by utilizing FFF, it is possible to create structures with magnetic anisotropy that can be influenced by print and infill orientation and geometry [4]. Unfortunately, current methods of 3D printing using MREs involve specialized equipment to mix the elastomer matrix and magnetic particulate during extrusion [5]. This could lead to issues, as the level of particulate dispersion has a significant impact on the consistency of physical properties in a polymer composite [6].

Solvent casting is a simple and powerful tool for dispersing particulate in polymer composites [7–9]. In comparison to the difficulty of mixing powders into a viscous polymer melt, solvent-casting provides the opportunity to vary the particulate addition and dispersion methods in order to control the degree of isotropy and minimize the clumping or agglomeration of the particulate by maximizing compatibility between the matrix and dispersed phase [7,10,11]. Maximizing the degree of dispersion of magnetic particles throughout the matrix is key to achieving consistency in both the mechanical and rheological properties of an MRE [6]. Furthermore, the ease of casting, being performed here at 85 °C and ambient pressure, makes solvent-casting an advantageous method for creating thermoplastic MRE composites.

In this study, we investigate the production of an MRE using the conventional method of solvent-casting and evaporation, focusing on the ability to control the level of particulate dispersion by altering addition method, particulate type, and particulate loading. Iron and magnetite (Fe_3O_4) particulates were introduced at increasing particulate loadings using both dry addition of particulate and wet addition, involving the pre-suspension of particulate in solvent prior to addition to the composite. Transmitted light microscopy was employed to observe the level of dispersion achievable by each method.

2. Materials and method

2.1. Materials

Uncolored NinjaFlex® polyurethane elastomer pellets were supplied by Fenner Drives (UK). Iron (<150 μm, hydrogen reduced, >98% purity) and Magnetite (Fe_3O_4, 2–4 μm, >99% purity) powders were purchased from by Chemical Store Inc. (US). The solvent used for casting was dimethylformamide (DMF, anhydrous, 99.8% purity).

2.2. Solvent-casting thin films

Polyurethane (PU) films were prepared using the standard solvent-casting method. The PU pellets were dried at 75 °C for 24 h then dissolved in DMF at 85 °C with a ratio of 4 mL:1 g, initial solvent to polymer, after mixing for 4–6 h until a homogeneous solution was obtained.

For composite samples, magnetic particulate was dispersed throughout this polymer solution. Mass of magnetic particulate was calculated in order to achieve a specific weight percent of magnetic particulate to PU. These calculations can be seen in Eq 1,

$$m_{MP} = m_{PU} * (wt\%) \tag{1}$$

where m_{MP} is the mass of magnetic particulate to be added to the solution, m_{PU} is the mass of PU used, and wt% is the target weight percent of magnetic particulate for the composite. Using this equation, solutions were prepared using iron and magnetite powders to concentrations of 20, 30, and 40 wt% via both wet and dry addition. Once masses of particulate were measured out, they were manually stirred for several minutes in order to break up agglomerations that were pre-existing in the magnetic powders.

In the case of dry addition, magnetic particulate was sprinkled over the solution under constant mixing until fully dispersed. Wet addition involved the suspension of magnetic particulate in several mL of solvent followed by addition to the PU solution under constant mixing until fully dispersed. Care was taken to continue mixing the suspension thoroughly up until the point of addition to the PU solution in order to prevent the particulate from settling. Table 1 shows the amounts of each component used in the production of each sample type. The resulting solutions were cast into glass molds with a diameter of 63 mm and placed in a dehydrator, seen in Figure 1, housed in a fume hood, at 75 °C for 24 hours to drive off solvent. Samples were produced in triplicate in order to increase the statistical significance of findings.

Several drying methods were considered during preliminary testing in order to optimize the drying time of samples. The two primary methods that were considered were air drying at room temperature and the use of a dehydrator which operates at 75 °C to drive off solvent. The decision to use a dehydrator was made based on the decreased dry time of preliminary samples when compared to air drying at room temperature. Dry times were established by a distinct dark-to-light color change that occurred in preliminary samples.

Table 1. Each of the cases tested, including the amounts of components used, type of magnetic particulate, and addition method employed.

Case	PU Mass [g]	Particulate Mass [g]	wt%	Solvent Vol. [mL]	Particulate	Addition Method
a	1	0.2	20	4	Iron	Dry
b	1	0.3	30	4	Iron	Dry
c	1	0.4	40	4	Iron	Dry
d	1	0.2	20	4	Magnetite	Dry
e	1	0.3	30	4	Magnetite	Dry
f	1	0.4	40	4	Magnetite	Dry
g	1	0.2	20	4	Iron	Wet
h	1	0.3	30	4	Iron	Wet
i	1	0.4	40	4	Iron	Wet
j	1	0.2	20	4	Magnetite	Wet
k	1	0.3	30	4	Magnetite	Wet
l	1	0.4	40	4	Magnetite	Wet

Figure 1. The microscope used for light microscopy analysis (left) and the dehydrator used for drying of test samples (right).

2.3. Light microscopy analysis

The produced thin films were observed via transmitted light microscopy in order to quantify the degree of particulate clumping. Observation of the films was done on a Nikon Alphaphot YS transmission microscope, seen in Figure 1, with a magnification of $100\times$. At such magnification, individual clumps of particulate were visible. In order to minimize selection bias, a random, arbitrary region of each sample was selected to be photographed and examined. These images were processed in MATLAB, as seen in Figure 2, to clarify particulate boundaries and achieve the level of segmentation necessary in order to determine the area of the largest 20 individual clumps present in each image. In some cases, further manual segmentation was required in order to completely differentiate particulate clumps. If there were not 20 distinct, large clumps present in an image, such as the case shown in Figure 2, all large clumps were counted. This creates a natural bias for samples containing fewer clumps to have a larger average clump size; however, this did not affect the trends found between particulate loading and average clump size. Using these calculated areas, the average large clump size was determined for each sample.
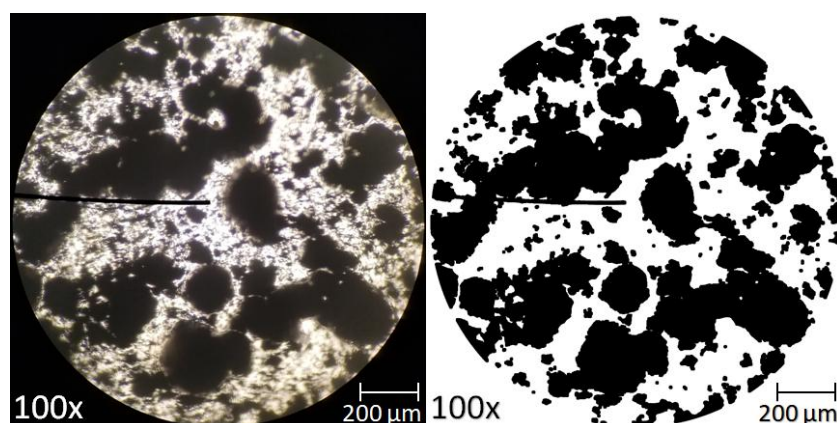

Figure 2. The initial image (left) and the image after processing in MATLAB (right). Note the removal of insignificant particles in the matrix and the clear definition of clump boundaries that is not present in the original image.

3.   Results and discussion

3.1. Solvent-casting

Solvent-casting the composite samples resulted in thin films with a final thickness between 0.15 and 0.20 mm and a diameter of 63 mm. This variation in thickness was the result of a subtle angle present in the hood housing the dehydrator but did not affect the level of particulate dispersion in the films. If consistent sample thickness was integral to the performance of the film, care would need to be taken to ensure that both the drying surface and sample were level while the solvent evaporates.

Dissolution of the PU in DMF created a viscous solution, comparable to honey at room temperature. As a result of this, the task of manually dispersing particulate through large volumes of polymer solution, such as those used in the production of bulk samples for further processing, proved difficult both in terms of manual mixing and determining when adequate dispersion had been obtained. This issue was exacerbated by the dry addition of particulate, which further increased the viscosity. Conversely, the wet addition of magnetic particulate introduced a significant volume of additional solvent along with the particulate, diluting the solution and decreasing the viscosity. In terms of ease of mixing and casting, the wet addition of particulate proved to be superior to dry addition as a result of the PU solution viscosity.

3.2. Particulate dispersion

It was observed that the level of particulate dispersion in the films was affected by several factors. These include: weight percent of particulate, type of particulate, and addition method. Figure 3 illustrates that as the loading of particulate increased from 20 to 40 wt%, the average large clump area increased with it. This increase is expected, as dispersing more particulate into the solution will naturally increase the density of particulate in the films, and therefore increase the size of clumps that form. This phenomenon is quite apparent in both Figure 3 and Figure 4, where it can be observed that while clump size increases as particulate loading, there is also simply more total particulate present in each image as weight percent of particulate increases.

It is also apparent that dry addition of particulate led to larger clump areas than wet addition in all cases. One advantage of wet addition is that by wetting the surface of the particulate with the solvent used to create the polymer solution prior to addition to the polymer solution, it may be possible to increase the compatibility between the surface of the particulate and the polymer matrix [11]. This increase in compatibility prior to addition to the polymer solution may result in more interaction between particulate and matrix, resulting in less tendency for particles to agglomerate. Although there will be interaction between solvent and particulate in the polymer solution after addition of the particulate for both addition methods, wet addition allows for thorough exposure of the particulate surface to solvent before it interacts with the PU matrix. Furthermore, the introduction of additional solvent during the wet addition of particulate serves to decrease the viscosity of the solution, as noted previously, easing the process of mechanically distributing the particulate during manual mixing. This ability to increase particulate-polymer compatibility and decrease the total PU solution viscosity gives wet addition a two-fold superiority over dry addition of the particulate.
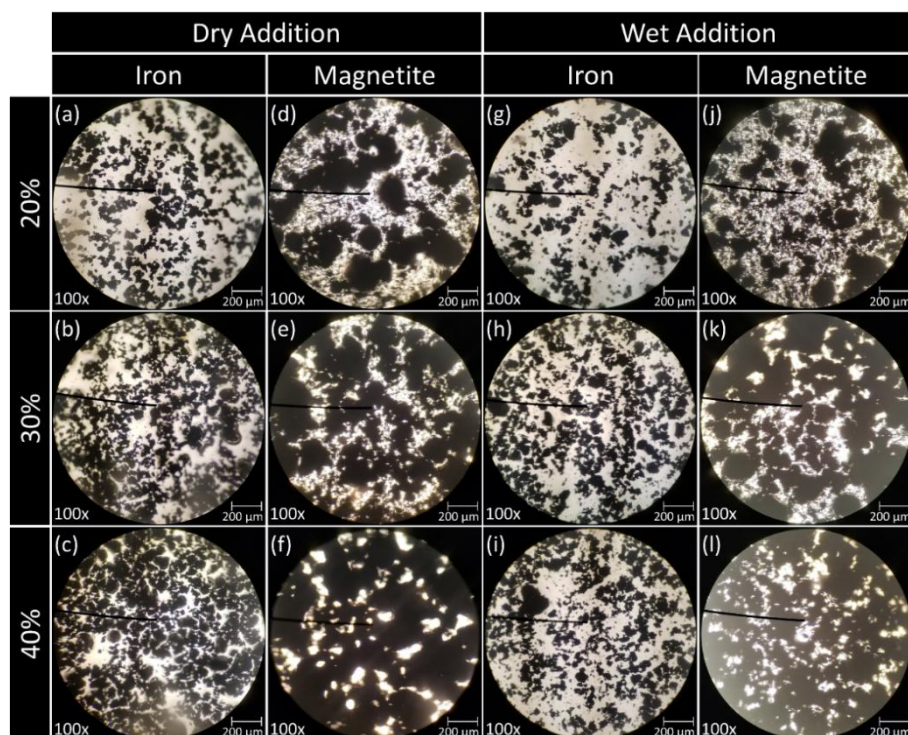
Figure 3. Images taken of a sample from each case. Note that as particulate loading increases, it is apparent that more and larger clumps are present in the samples. It is also evident that samples containing magnetite powder exhibit more dramatic clumping than those containing iron powder.
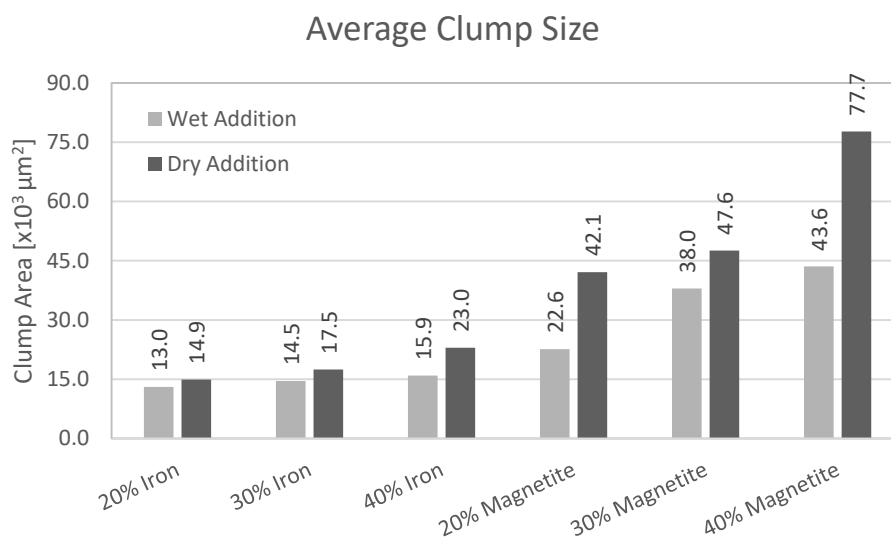

Figure 4. The particulate clump area for each sample case. Several trends are able to be established: average clump area increases for all cases as particulate loading increases, dry addition of particulate results in larger average clump area than wet addition in all cases, and magnetite samples exhibited more dramatic particulate clumping than iron samples in all cases.

The final distinction between cases is that of particulate type. The size of clumps present in magnetite composite samples was higher than that found in their iron counterparts. The factors behind the disparity in clumping of the two particulate types can be attributed primarily to forces present in magnetite particles and secondarily to a number of physical differences between the particulate types used. The primary cause of the additional agglomeration present in the magnetite composite samples is the strong magnetic attraction, van der Waals forces, and relatively high surface energy present in individual magnetite particles [12]. The magnetic forces are more prevalent in magnetite as a hard-magnetic material which has higher remnant magnetization than iron. Van der Waals forces between magnetite particles are also stronger than those between iron particles due to uncompensated surface charges from the ionic nature of Fe_3O_4 as opposed to metallic iron. The presence of these forces in magnetite particles gives them the propensity to agglomerate due to magnetic attraction, and in order to reduce the area of their surface that is interacting with the PU. This often incentivizes the use of polymer coatings or surfactants when dispersing magnetite nanoparticles. Without the use of surfactants, these forces result in a distinctly different mode of agglomeration in magnetite samples than in iron composite samples. This phenomenon can be observed by comparing samples seen in Figure 3a,d, in which the magnetite samples clearly demonstrate both a higher degree and different mode of agglomeration when compared to the iron samples. As these effects are the driving factor for agglomeration in magnetite composite samples, the ability of wet addition to increase the compatibility between the surface of the magnetite particulate and the polymer solution causes the dispersity improvement of wet addition to be more significant in magnetite samples than in iron samples. In fact, the improvement in dispersion of the iron particulate is very minor in comparison to the magnetite particulate, as iron particulate is already comparatively well dispersed in PU.

Secondarily, there are discrepancies between both the particulate size of the magnetite and iron powders, as well as their densities. The purchased magnetite powder had a size range of 2–4 μm while the iron particulate was nominally <150 μm. This difference makes agglomeration more prevalent in the magnetite powder, because powders with smaller particle size are more prone to clumping or agglomeration effects [13]. Considering the material densities, iron has a density of 7.87 g/cm^3 and magnetite has a density of 5.15 g/cm^3. This means that for the same weight percent infill there will be approximately 50% more volume of magnetite than there would be of iron. Similar to increasing the particulate loading, this discrepancy results in there simply being a larger volume of magnetite than iron in equivalent weight percent samples. Together, the forces present between magnetite particles and the physical discrepancy between the iron and magnetic particulates used result in significantly increased levels of agglomeration in magnetite samples when compared to equivalent iron samples for both addition methods.

4. Conclusion

Thin films of TPU composites containing iron and magnetite particulate were manufactured to examine the control over the degree of particulate dispersion that can be achieved when utilizing the solvent-casting method. The effects of increasing particulate loading, altering addition method, and changing particulate type were examined. The observations of each of these variables can be summarized as follows: (1) The average particulate clump size increases with increasing particulate loading. This result is quite natural, as higher particulate loadings simply have more particulate in

them that can agglomerate. (2) Wet addition of particulate resulted in an improvement to particulate dispersion when compared to Dry addition. This is the result of two different effects. First, exposure of the particulate to solvent prior to addition to the polymer solution increases the compatibility between the particulate surface and the polymer matrix, which results in a decreased tendency for particulate to agglomerate. Additionally, the volume of solvent added alongside the magnetic particulate serves to decrease the viscosity of the polymer solution, easing the process of dispersing particulate. (3) Magnetite particulate composites exhibited significantly greater clump sizes than iron particulate composites, which were well distributed in PU in all cases. Again, this is the result of several effects. The primary cause of the increased agglomeration in magnetite samples can be attributed to strong magnetic attraction, van der Waals forces, and relatively high surface energy present in individual magnetite particles. The presence of these forces in only the magnetite particulate results in significantly more agglomeration being present in magnetite samples when compared to iron samples. Additionally, the smaller particle size of the magnetite (2–4 μm) when compared to iron (<150 μm) causes the magnetite particulate to be more prone to agglomeration and the decreased density of magnetite (5.15 g/cm^3) compared to iron (7.87 g/cm^3) results in magnetite samples having a higher volume of particulate. Together, these effects lead to a dramatic increase in the level of agglomeration present in magnetite samples when compared to iron samples.

Understanding how these various processing techniques affect the resulting dispersion of solvent-cast composites will allow for increased control over the magnetic and mechanical properties of MREs produced using the solvent-casting method, which is crucial in applications where isotropy is paramount, such as FFF. In the future, the use of surfactants and polymer coated particles may also be explored as a method of increasing the level of dispersion attainable when utilizing solvent-casting as a method of producing MREs.

Conflict of interest

All authors declare no conflicts of interest in this paper.

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