

Issues Associated with the Development of a Water Soluble Support Material for use in Extrusion Freeforming & Fused Deposition Modelling

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ABSTRACT

Extrusion freeforming (EFF) and Fused Deposition Modelling (FDM) are promising techniques for fabricating complex shaped prototypes from a variety of engineering materials. Both techniques build prototypes by depositing and solidifying free standing layers of molten thermoplastic material upon one another until the final part results. Unfortunately many prototypes have complicated geometries (i.e. numerous overhangs or internal features) such that they are not easily fabricated by these techniques without the assistance of a fugitive material to support the freeformed layers. This paper discusses the development and characterization of water soluble thermoplastic support materials for use in EFF & FDM fabrication processes.

INTRODUCTION

Extrusion Freeforming (EFF) & Fused Deposition Modelling (FDM) processes are established freeforming techniques capable of fabricating complex shaped prototypes by the sequential deposition and solidification of molten thermoplastic layers upon one another until the final part results. Unfortunately it is often difficult to accurately fabricate complex geometry prototypes having numerous overhangs by these techniques without the assistance of a fugitive support material to prevent slumping of the freeformed layers prior to their solidification. Current freeforming technology utilizes a support material that is initially deposited and later mechanically removed from the completed prototype. This type of fugitive support has limited utility, however, when fabricating fine featured, intricate prototypes due to its labor intensive removal process. Consequently, it is advantageous to develop fugitive support materials which are removable by solvent means. It was therefore decided that water soluble support materials would be developed since water is a non solvent for most freeformable thermoplastics coupled with its ready availability and minimal environmental concerns.

A review of the polymer literature reveals that most common commercial water soluble polymers have the drawback of either exhibiting inferior melt stability (i.e. polyvinyl alcohol & polyvinylpyrrolidone) or rapid crystallization and low cohesion (i.e. polyethyleneoxide) (1). For these reasons, most commercial water soluble polymers are not easily freeformable. Poly 2-ethyl-2-oxazoline (PEOx), however, is a lesser known commercial water soluble thermoplastic which does not suffer from the above drawbacks. PEOx is also an amorphous homopolymer ($T_g = \text{approx. } 70^\circ\text{C}$) that has been shown to possess high cohesion as well as adhesion to a wide variety of substrates (2). Furthermore, light scattering studies conducted by Chen et al. on solutions of the polymer

suggest that PEOx is less strongly solvated and therefore not as sensitive to water compared to common organic solvents (3). efforts were therefore focused upon developing PEOx based water soluble support filament feedstocks which could be processed using a conventional Stratasys 1600 FDM Modeller or high pressure EFF extruder apparatus. Since the processing criteria and materials property requirements for FDM compatible feedstocks are more stringent than EFF materials, greater discussion will be made of the former.

Besides exhibiting water solubility, several other considerations should be factored into account when developing FDM compatible filament feedstock. First, the filament should possess sufficient elastic modulus coupled with flexural strength such that the filament feeds uniformly through the FDM apparatus dispensing head without buckling or fracturing. Furthermore, the feedstock should not undergo significant changes in its rheological properties or swell when exposed to ambient relative humidities ranging from 30 to 70 percent.

EXPERIMENTAL

All water soluble support raw material batches were formulated using a Brabender mixer operating at a 60 rpm mixing speed and 140 °C temperature. After formulation, the water solubility of the batches was evaluated by measuring the amount of time require to dissolve an 8g sample in 80 ml water. Filament specimens measuring 3 ft. in length by 0.070 inches in diameter were subsequently extruded from these batches using a Haake Rheomix Model 103 Microextruder. Following extrusion the filament lengths were fed into a Stratasys 1600 FDM modeller and simple test bars were subsequently freeformed from the material. The microstructure of several filaments was characterized using a Hitachi Model S-4500 Field Emission Scanning Electron Microscope. All SEM samples were prepared by first fracturing the filament followed by sputter coating a conductive Au-Pd coating on the fractured surface prior to their characterization. Energy Dispersive X-ray Spectra were obtained from the blend microstructures using a Noran Model 5500 Spectrometer having a light element detector. Comparison was made between the intensity of the individual sample spectral peaks with those of the sputtered Au-Pd coating standard. The thermal properties of select blend compositions were determined using a Perkin Elmer Model 7 Differential Scanning Calorimeter (DSC) apparatus operating at a 20 °C/minute heating rate while scanning through a 30 to 120 °C range. Finally optimized filament support material was used in the FDM fabrication of a prototype asthma inhaler diaphragm made on a Stratasys 1600 Modeller from polyacrylonitrile-butadiene-styrene (ABS) modelling material. (See Fig. 5.) The FDM modeller operating parameters were similar to those employed in the fabrication of conventional polymer prototypes with 0.010 in. slice interval, .070 in. road width, 70 °C modelling envelope, & 270° C ABS polymer extrusion temperature.

RESULTS

Initial research efforts focused upon blending PEOx with sufficient plasticizer and talc filler using a Brabender mixer in an effort to decrease the polymer melt viscosity

while simultaneously increasing the compression strength and creep resistance of the material. Candidate formulations were then extruded into filament test specimens measuring 0.070 ± 0.002 inches in diameter by 3 ft. in length using a Haake Rheomix Model 130 microextruder. Despite the fact that these filaments were initially successfully used as processible feedstock for a conventional Stratasys Modeller, the specimens swelled significantly and proved unusable upon prolonged exposure to a humid atmosphere ($> 40\%$).

Consequently research efforts were then directed towards modifying the PEOx formulation such that its sensitivity towards humidity was decreased. This was accomplished by blending PEOx with water insoluble polymers. Several PEOx blends were then formulated using a Brabender containing between 1 and 15 vol. % of both polystyrene-co-acrylonitrile (SAN) and polyphenyleneoxide (PPO) resins. SAN and PPO were blended with PEOx due to their water insolubility coupled with their reported ability to form miscible blends with the polymer (4). Filament specimens of these polymers were also prepared and evaluated as feedstock in the Stratasys FDM Modeller. Even though these PEOx blend specimens were shown to be FDM compatible and less strongly effected by humidity (particularly at SAN & PPO concentrations exceeding 10 wt. percent), the blends were insoluble in water. The insolubility of these blends was pronounced even at low SAN & PPO concentration in the blend (< 1.5 wt. %).

Blends were also formulated using PEOx and 5 to 30 volume percent of a water insoluble styrenic copolymer. These blends differed from the former in that the styrenic phase was believed to be immiscible in PEOx. A compatibilizer was added to the formulation to enable adhesion between the two phases in the blend. Since the styrenic copolymer had a reported glass transition temperature greater than the FDM apparatus modeller heated envelope but below the PEOx extrusion temperature, it was believed that the styrenic phase would increase the overall softening temperature of the blend while concurrently enhancing its creep resistance at the modeller envelope operating temperature. FDM filament specimens were fabricated and were found to be readily processible by a conventional Stratasys FDM Modeller. Table I below depicts a typical PEOx/Styrenic blend composition.

Table I Typical Freeformable PEOx/Styrenic Blend Composition

Component	Concentration (Vol. %)
Talc Filler (submicron sized)	15
Poly-2-ethyl-2-oxazoline	45
Polystyrene copolymer	30
Plasticizer	7.0
Compatibilizer	3.0

The above listed blend was characterized using both SEM and DSC. Figures 1 and 2 depict microstructures of blends containing 26 and 30 volume percent of styrenic

copolymer phase respectively. Both microstructures contain spheres having an average diameter of 2 microns uniformly dispersed throughout a continuous phase. Since there appears to be a higher concentration of spheres in Fig. 2 compared to Fig. 1, it is believed that these spheres are composed of the styrenic copolymer. SEM EDS microprobe analysis spectra of the continuous versus spherical phases depicted in Figure 3 present in the blend containing 26 volume percent styrenic phase suggest that the talc $\{Mg_3Si_4O_{10}(OH)_2\}$ filler is segregated to the PEOx phase. This is expected since PEOx has been shown to have a high affinity for siliceous mineral surfaces (5). Further support suggesting the presence of a two phase polymer blend in these samples can be found in the DSC results obtained from the sample blend containing 26 volume percent styrenic copolymer whereby two glass transition temperatures were measured in the sample as seen in Figure 4. The onset of the first Tg was measured at 45.1° C while the latter was at 113°C . These compare favorably with the Tg data obtained for the pure styrenic copolymer, compatibilizer, and blend composed of all components minus the styrenic material listed in Table II below. From these results it can be seen that there is no significant difference in the Tg of the blend components compared to its individual components.

Table II DSC Results for PEOx Blend & Individual Components

	Glass Transition Temp. (°C)
PEOx/26 vol. % Styrenic Blend	45.1, 113
PEOx Blend without Styrenic	48.7
Styrenic Copolymer	116
Compatibilizer	52.2

CONCLUSIONS

PEOx/Styrenic copolymer blend has been successfully developed as a fugitive FDM water soluble support material. The blend is composed of a continuous phase of PEOx containing talc along with a discrete styrenic copolymer phase uniformly dispersed throughout the major phase as spherical droplets measuring approximately 2 micrometers in diameter. The similarity in Tg values between the blend and its pure constituent components suggest that there is minimal intersolubility between each of the blend components. Future research will focus upon quantitatively determining the creep and stress relaxation properties of these blends.

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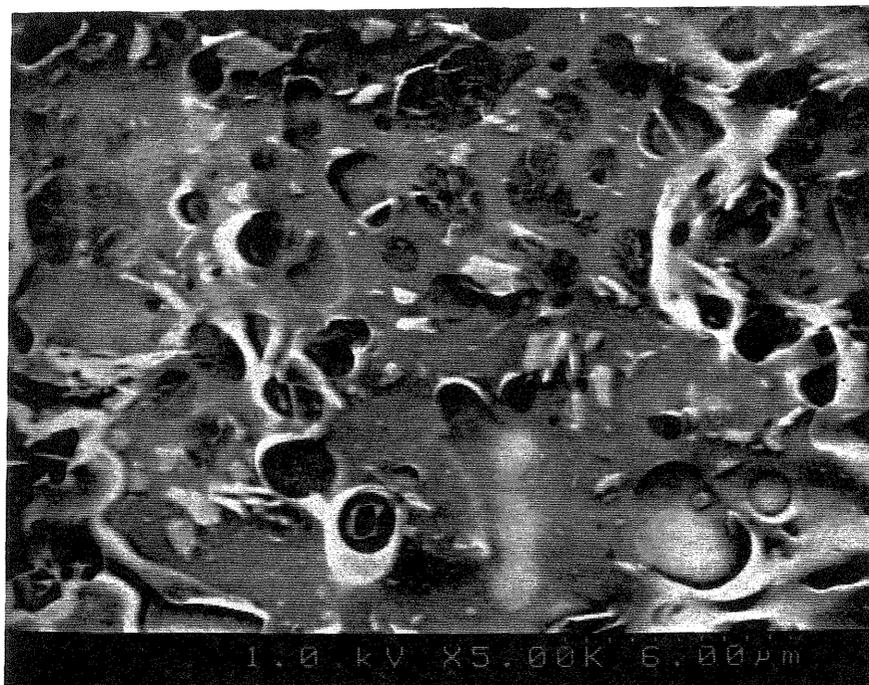


Figure 1. SEM micrograph of PEOx blend containing 26 vol. % styrenic copolymer

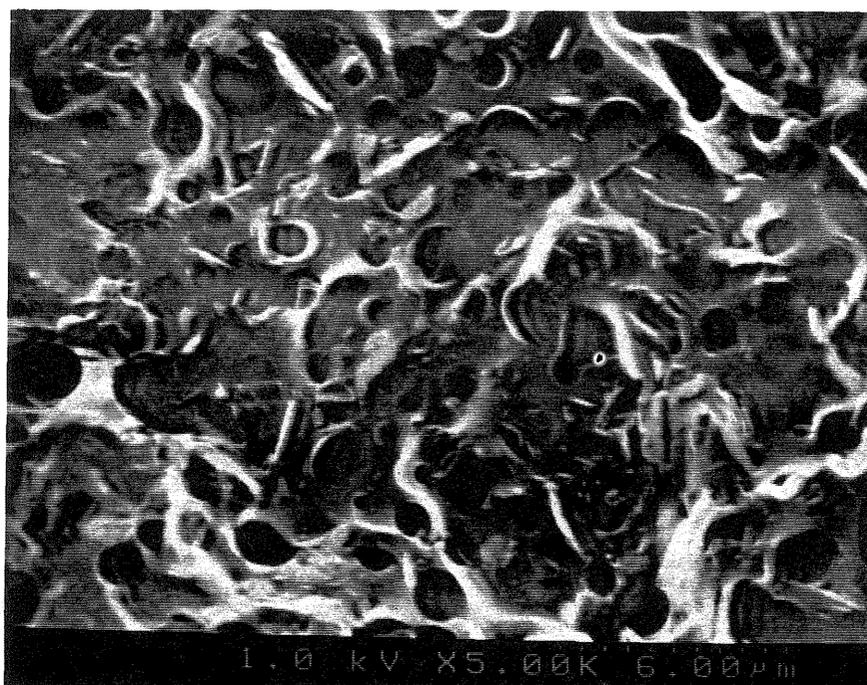


Figure 2. SEM micrograph of PEOx blend containing 30 vol. % styrenic copolymer

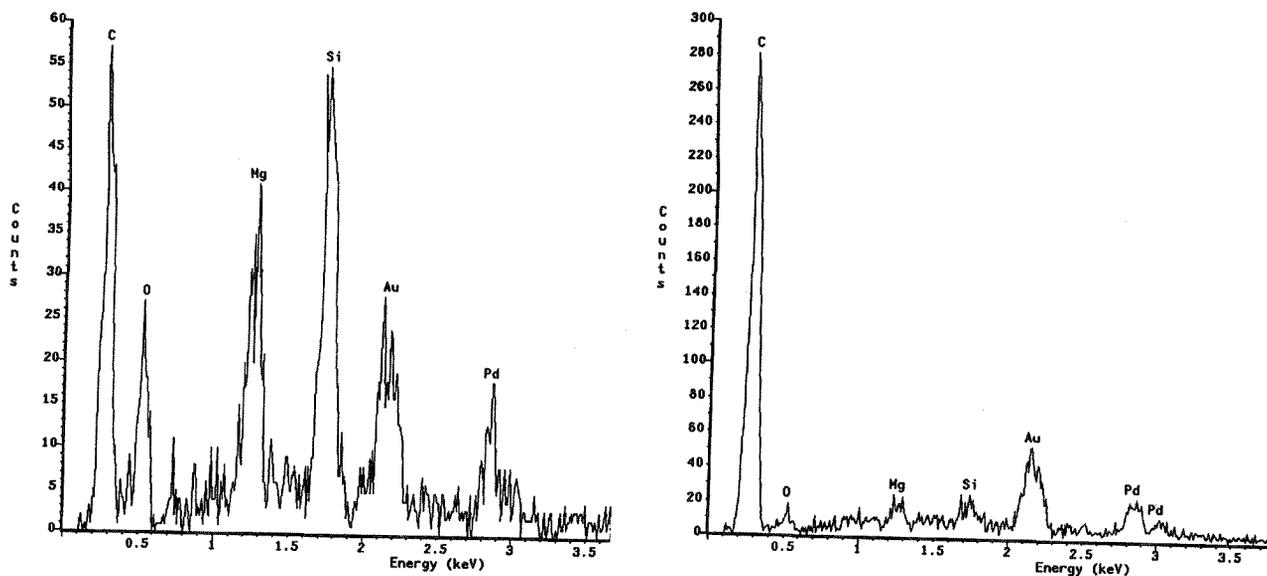


Figure 3. SEM EDS spectra of PEOx blend containing 26 vol. % styrenic copolymer microstructure matrix (left) & spherical phase (right)

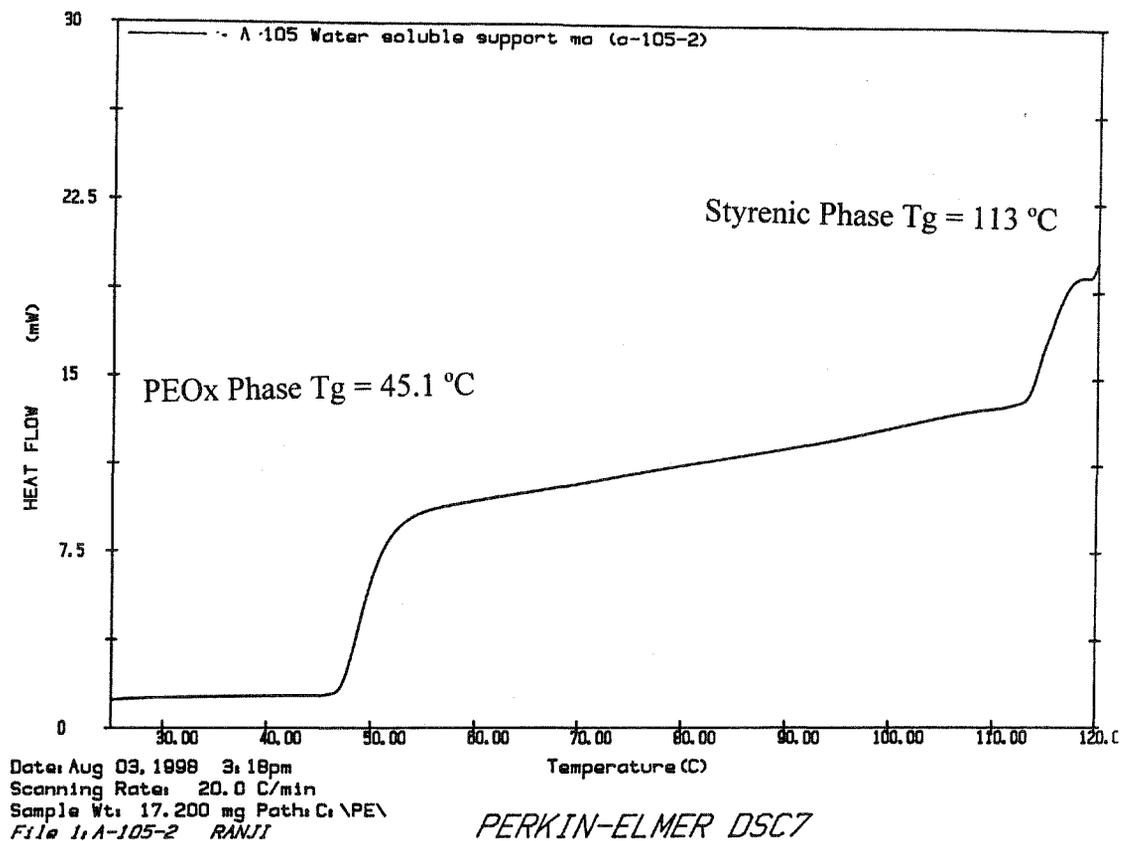


Figure 4. DSC plot obtained from PEOx/26 vol. % styrenic copolymer

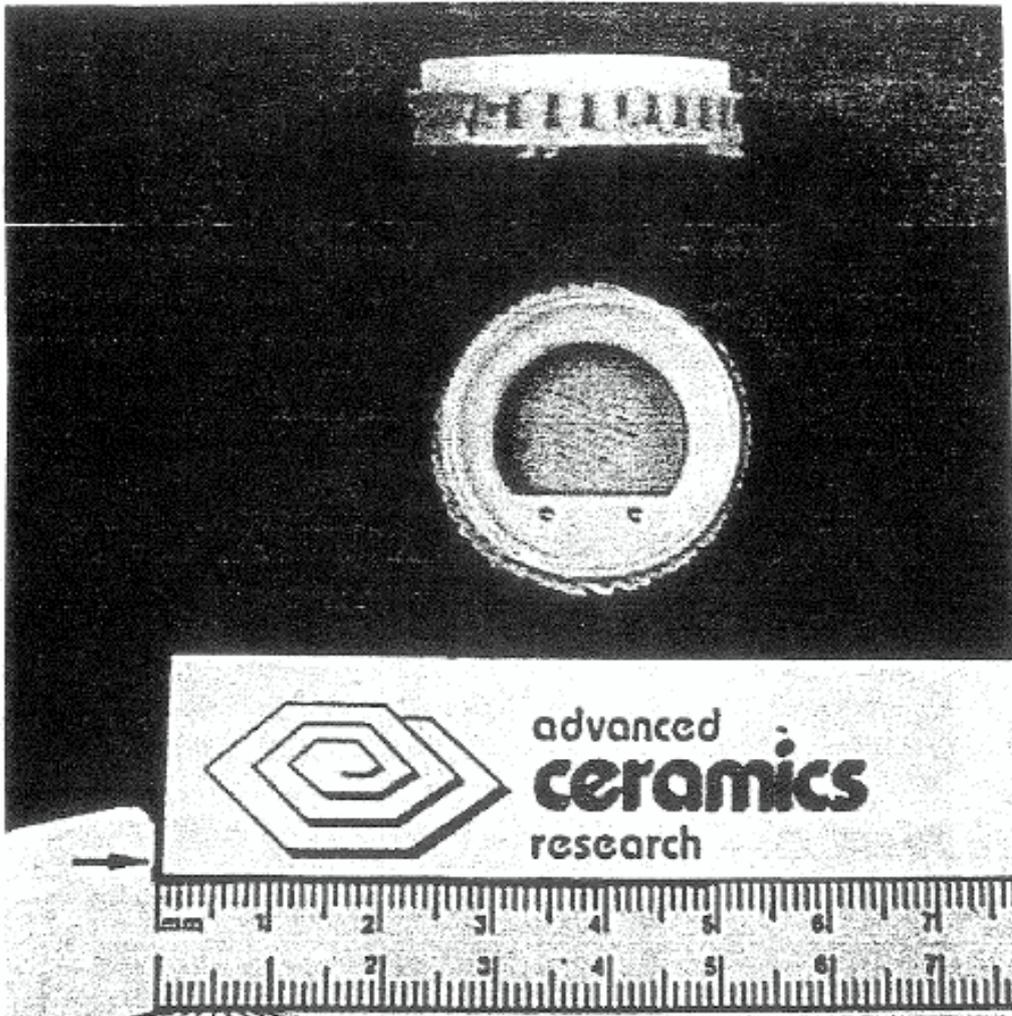


Figure 5. Photograph of P400 ABS Inhaler Diaphragm Prototype freeformed using PEOx/Styrenic water soluble support by Stratasys 1600 Modeller

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