Research into a novel support material for jetting based RM process

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Abstract

Jetting of caprolactam is a new Rapid Manufacturing process currently in the early phases of research at Loughborough University. Support material is required to successfully build a part using this method. This work is therefore, aimed at finding a suitable support material for jetting of caprolactam. Pluronic F-127 with a non aqueous solvent was investigated using different experimental techniques such as heating and cooling between 25 to 150^{0}C, Fourier Transform Infrared Spectroscopy and Polarization Microscopy and the possibility of use of these systems as a support material is discussed. The results suggested that when Pluronic F-127 in ethylene glycol is heated, it does not form a gel at concentrations lower than 25% (w/w) whereas at 25%, a gel state was observed near 50^{0}C. All concentrations studied formed a white wax like solid upon cooling due to a changed conformational structure of PEO chains. Although, a gel/solid state was not observed at high temperatures, these compositions can provide a possible support material for a low temperature (i.e. 25^{0}C) build environment.

Introduction

Support material plays an important role during layer-by-layer manufacturing of three dimensional parts via some of the commercially available additive manufacturing (AM) processes. A support material not only facilitates the removal of the part from the build platform after its completion but it also enables manufacturing of intricate features such as downward facing curved surfaces, overhanging features, holes and cavities. Also, the support material provides the resistance against the tendency of a model to deform due to applied forces during build [1,2].

Most of the jetting based AM processes such as Multi-Jet Modelling, PolyJet and Solidscape 3D Printing make use of support material during manufacture of parts and these support materials are jetted in a similar way as the build material. Jetting of caprolactam is a novel AM process which is currently under research at Loughborough University. The process utilizes inkjet heads to deposit liquid droplets of caprolactam which polymerize into nylon after being jetted. Details of this process have been discussed elsewhere [3,4].

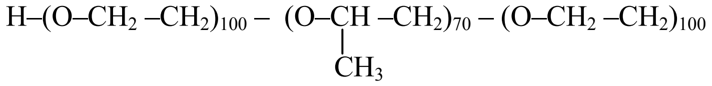
The aim of this project is to find a suitable support material for the jetting of caprolactam and evaluate its jettability. As with the above mentioned jetting based RM processes, the support material will be jetted using inkjet heads and thus should be liquid with low enough viscosity (i.e. around 50 mPa.s) at or below 80^{0}C which is the maximum allowed temperature for the inkjet head being used for the project. The selected material for the research is Pluronic F-127, a block copolymer of polyethylene oxide (PEO) and polypropylene oxide (PPO), due to its reverse thermal gel formation abilities in water. At low temperatures (usually lower than 15^{0}C), both PEO and PPO blocks are soluble in water and are present in the form of polymer chains called unimers. At higher temperatures (usually above 15^{0}C) PPO becomes less soluble in water (i.e. hydrophobic) whereas the PEO remains soluble. At or above a certain concentration, called the critical micelle concentration (CMC), these unimers convert to micelles upon increasing the temperature above a certain value called the critical micelle temperature (CMT). This micelle formation is caused by the dehydration of the PPO blocks at high temperatures [5]. Upon further increasing the temperature to a value called the gel temperature (T_{gel}), these micelles come into contact with each other and micelle entanglement takes place. This entanglement is caused due to the tieing of PEO chains between adjacent micelles and the micelles arrange themselves into lyotropic liquid crystalline structures (cubic, hexagonal and/or lamellar). The formation of crystalline structure restricts the movements of the micelles and thus a gel phase is formed [5-7]. Water is the most commonly used solvent for reverse thermal gel formation. However, water presents difficulties in terms of its boiling point which is below the expected build envelope temperature (i.e. 150^0C) and because it inhibits the polymerization of caprolactam into nylon, so a novel combination of Pluronic F-127 and ethylene glycol was investigated.

Experimental

Materials

Pluronic F-127 (see table 1 for properties) was purchased from BASF and ethylene glycol was purchased from Fisher Scientific. Both were used as received without any further purification.

Table 1. Properties of Pluronic F-127 supplied by the manufacturer (BASF)

Chemical Structure	 $H{-}(O{-}CH_2{-}CH_2)_{100}{-}(O{-}\underset{CH_3}{\underset{\vert}{CH}}{-}CH_2)_{70}{-}(O{-}CH_2{-}CH_2)_{100}$
Molecular Weight	12,600 g/mol
PEO Content	70% of total molecular weight

Sample Preparation

Four different samples were prepared with concentrations ranging from 10% to 25% (w/w) F-127 in ethylene glycol in increments of 5%. Samples were prepared by mixing weighted amount of F-127 in ethylene glycol and the sample size was restricted to a total of 50 g for each sample. Mixing was performed using a magnetic stirrer. The samples were allowed 24 hours of continuous stirring and after stirring, they were kept in a refrigerator (approximately 4^0C) to ensure stabilization of the mixtures.

Sample Heating

A small amount (approximately 5-6 g) of each sample was taken in sample tubes (inner diameter 23 mm) to perform heating experiments to observe gel formation or any other change in the state of the samples upon increasing the temperature. Heating was performed using an oil bath and a hot plate. An average heating rate of 5^0C/min was used and samples were heated from 25 to 150^0C. Qualitative observations (i.e. change in the state of samples) were made by tilting the sample tubes and a gel state was identified when no meniscus movement was observed upon tilting the tube. Samples were allowed to cool back to the initial temperature (25^0C) under natural cooling and observations were also made during cooling for any change in the state of each sample.

Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy of ethylene glycol, Pluronic F-127and the four samples before heating and after heating was performed. A Shimadzu FTIR-8400S spectrometer was used to analyse all the samples with a standard deuterated L-alanine doped triglycine sulphate (DLaTGS) detector. Spectral resolution was 4 cm^{-1} and infrared (IR) spectra were recorded by scanning 64 times for each measurement. Apart from the Pluronic

F-127, which was in the form of flakes, all the other samples were sandwiched between two round (25 mm diameter x 4 mm thick) sodium chloride (NaCl) crystal windows. The IR spectrum for Pluronic F-127 was obtained by using the Attenuated Total Reflectance (ATR) technique with a diamond crystal.

Hot-Stage Microscopy

The hot stage microscopic examinations of the Pluronic F-127 powder and Pluronic F-127 in ethylene glycol solution with the highest concentration (i.e. 25%) were performed using a Leica DM/LM microscope (crossed polarisers) with an objective lens of magnification 10x. A total magnification of 100 times was used to observe the two samples. Each sample was placed inside a hot stage (Mettler Toledo FP82HT) which was mounted on the microscope slide. A Mettler Toledo FP90 central processor was used to control the temperature during microscopic examination of the samples. The samples were heated from 25 to 100^{0}C using a heating rate of 5^{0}C/min then kept at 100^{0}C for 1 min. Samples were cooled at natural cooling rate. Images were captured using a JVC colour video camera at 1 frame per second.

Results

Sample Heating

All four samples were turbid mixtures at room temperature (Figure 1.a) which reflected the insolubility of Pluronic F-127 in ethylene glycol. As the temperature was increased, the solutions started turning clear at around 35^{0}C and all the four samples were completely clear (transparent) solutions at 50^{0}C. No change was observed in either the colour or in the meniscus movement of the solutions upon increasing the temperature up to 150^{0}C (Figure 1.b). After reaching the highest temperature (i.e. 150^{0}C), the solutions were allowed to cool back to room temperature. As the solutions were cooled back, the 25% solution produced a clear, soft gel near 50^{0}C whereas the other three samples were liquid at this temperature (Figure 1.c). Further cooling to near 25^{0}C resulted in appearance of turbidity in all the four samples which resulted in a white coloured, soft (wax like) solid at 25^{0}C for all the four samples (Figure 1.d). The solid formed was readily soluble in water.

In order to observe the gel melting temperature, the 25% sample was reheated. The sample at the start of reheating was a white wax like solid. As the temperature was increased, it started turning turbid near 30^{0}C and was a clear gel near 40^{0}C. The gel melting was observed near 50^{0}C.

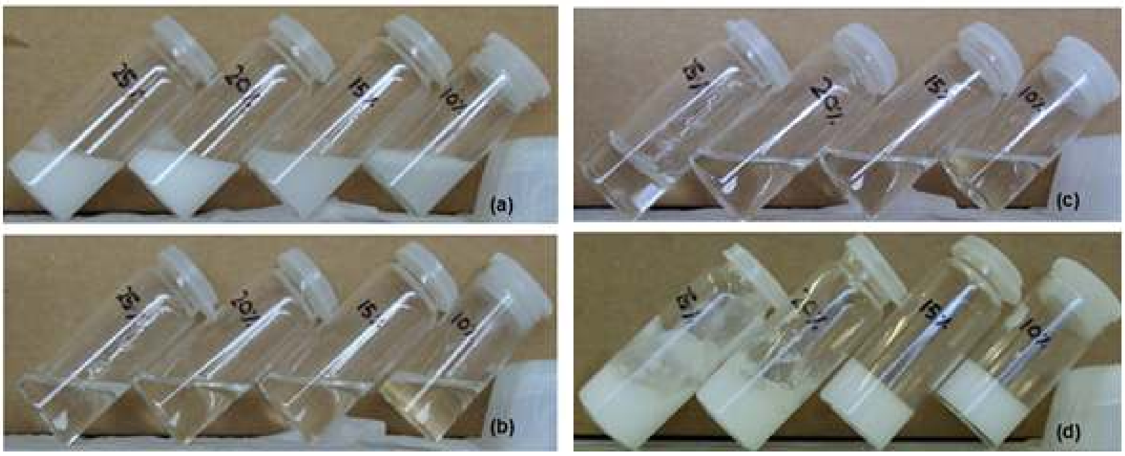


Figure 1. Pluronic F-127 in Ethylene Glycol samples at: (a) 20^{0}C (b) 150^{0}C (c) 50^{0}C, during cooling (d) 25^{0}C, cooled back

FTIR Spectroscopy

Table 2 presents a summary of the spectroscopic peaks obtained during the FTIR of the samples. Functional groups corresponding to each peak along with the component of the sample which relates to the peak are also presented in the table 2. Figure 2 depicts the IR spectra of F-127, ethylene glycol, and the 25% sample before and after heating.

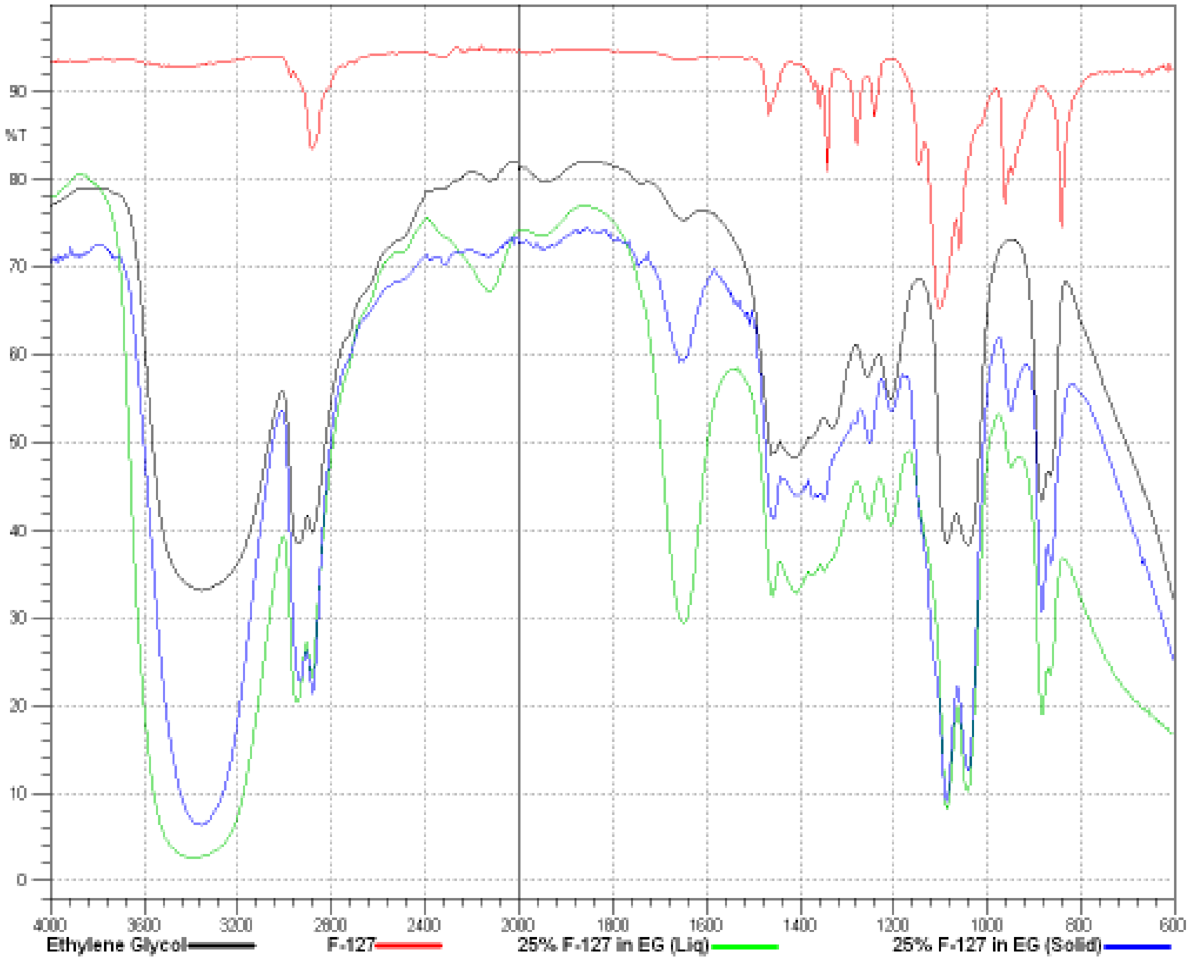


Figure 2. FTIR spectra of samples

Table 2. Peaks obtained for different samples using FTIR spectroscopy

Ethylene Glycol	**Pluronic F-127**	**Pluronic – Ethylene Glycol solutions**								**Functional Group Assignment**[1]	**Peak Related to**[2]
		Liquid				**Solid (after heating)**					
		10%	**15%**	**20%**	**25%**	**10%**	**15%**	**20%**	**25%**		
	840									CH_2 rocking	PEO (C),PPO
864		864	864	864	864	864	864	864	862	CH_2 rocking	EG
883		883	883	883	883	883	883	883	883	CH_2 rocking	EG
	947	943	945	947	949	949	950	949	949	CH_2 rocking	PEO (A), PPO
	960	964	962	964	962					CH_2 rocking, C-O-C stretching	PEO (C)
1041		1039	1041	1043	1043	1041	1043	1041	1041	CH_2 rocking, C-O-C stretching	EG
	1058									CH_2 rocking, C-O-C stretching	PEO (C)
1085		1085	1082	1089	1085	1085	1085	1085	1087	C-O-C stretching	EG
	1101									C-O-C stretching	PEO (C), PPO
	1145	1149	1147	1149	1147					C-O-C stretching, C-C stretching	PEO (C) PEO (A)
1205		1205	1205	1205	1205	1205	1205	1205	1203	CH_2 twisting	EG
	1242	1244	1242	1242	1244					CH_2 twisting	PEO (C), PPO
1255		1253	1253	1253	1253	1251	1251	1251	1251	CH_2 twisting	EG
	1278	1278	1278	1278	1278				1280	CH_2 twisting	PEO (C), PPO
1330	1342	1342	1342	1342	1342	1346	1340	1340	1348	CH_2 wagging	EG, PEO (C),PPO
	1359	1359	1359	1359	1359					CH_2 wagging, C-C stretch	PEO (C)
	1373	1371	1371		1371	1371	1371	1373	1373	CH_3 symmetric deformation	PPO
1411		1410	1410	1410	1410	1410	1410	1410	1406	CH_2 wagging, C-C stretching	EG
1452	1454	1454	1454	1456	1454	1454	1454	1454	1454	CH_2 scissor	EG, PEO (C), PPO
	1465	1464	1462	1464	1464					CH_2 scissor	PEO (C)
	2740										PEO (C), PEO (A)
2877	2879	2877	2879	2879	2879	2877	2877	2877	2877	Symmetric C-H stretch of CH_2	EG, PEO (C),PPO
2939		2937	2937	2939	2945	2939	2941	2937	2933	Antisymmetric C-H stretch of CH_2	EG
	2970									Antisymmetric C-H stretch of CH_3	PPO

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[1] Assignments are based on references [8-14]

[2] PPO = polyethylene oxide, PEO(C) = Crystalline polyethylene oxide, PEO(A) = Amorphous polyethylene oxide, EG = Ethylene Glycol

Hot-Stage Microscopy

Figures 3(a) and 3(b) depict the micrographs of the 25% sample at 25 and 40^{0}C showing the presence of crystalline structure at these temperatures while Figures 3(c) and 3(d) respectively represent the onset and completion of dissolution of Pluronic F-127 in ethylene glycol. Figures 4(a) – 4(d) represent the onset of crystallisation for the sample starting near 28^{0}C (Figure 4(b)) up to complete crystallisation at 25^{0}C. Similarly, The reason for two different micrographs (i.e. Figures 4(c) and 4(d)) at 25^{0}C for F-127 dissolved in ethylene glycol is that the crystallisation took place slowly so the micrograph (Figure 13.d) was taken after the sample was kept for approximately 20 minutes at 25^{0}C.

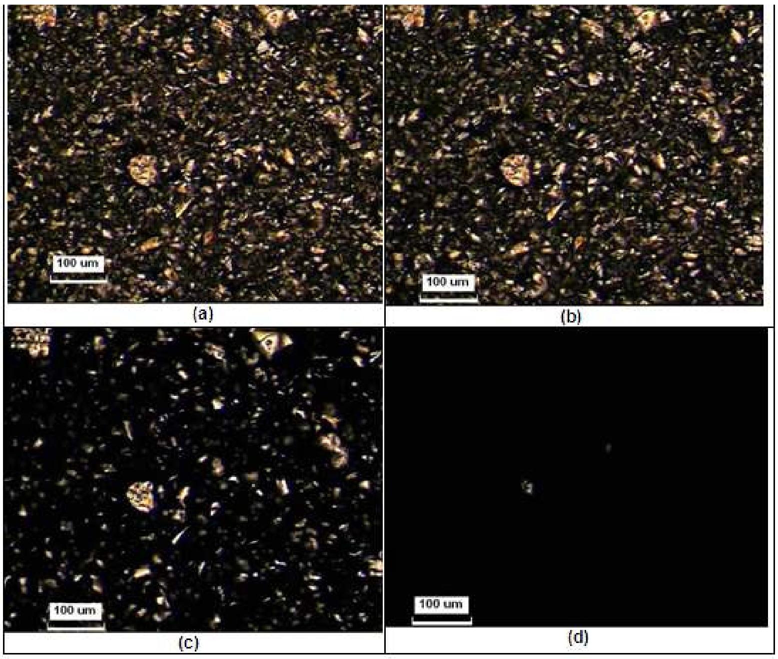

Figure 3. Micrographs of 25% Pluronic in Ethylene Glycol, heated at: (a) 25^{0}C (b) 40^{0}C (c) 42^{0}C, dissolution increased (d) 44^{0}C, completely dissolved

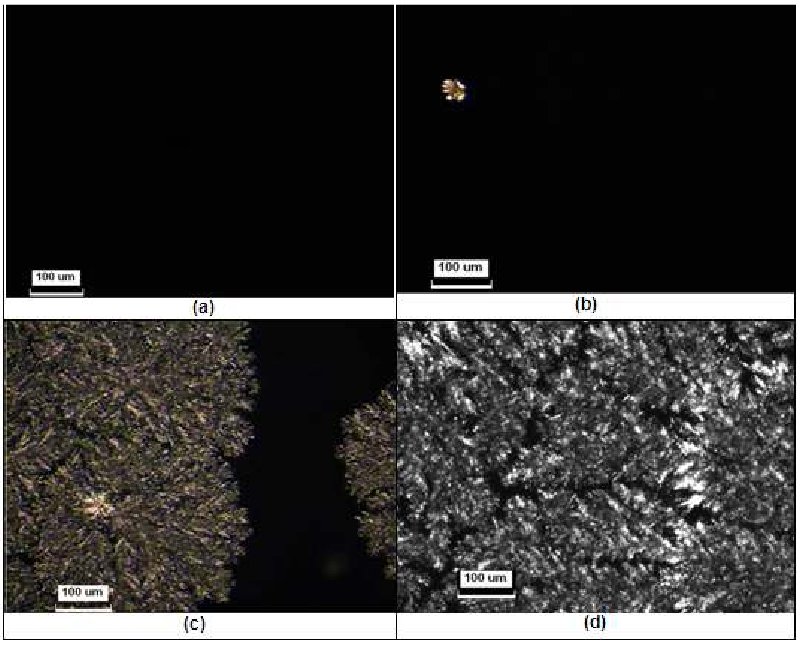

Figure 4. Micrographs of 25% Pluronic in Ethylene Glycol, cooled to: (a) 40^{0}C (b) 28^{0}C (c) 25^{0}C (d) 25^{0}C, after approximately 20 minutes

Discussion

The results showed that Pluronic F-127 did not form a gel upon heating in ethylene glycol. However, for 25% concentration, a gel state was achieved at 50^0C during cooling and the gel was melted at 50^0C during reheating. As depicted in Figure 1(a), and Figure 3(a), F–127 is partly soluble in ethylene glycol resulting in a turbid mixture. This is also confirmed by the FTIR spectra as some of the peaks related to F-127 (i.e. 1058, 1101, 2740 and 2970 cm^{-1}) disappear in the samples but most of the peaks remain in the liquid samples.

As the samples were heated, the solubility is increased and the Pluronic is dissolved completely between 40 – 50^0C which is evident from the Figures 1(b), 3(c) and 3(d). The gel formation shown by 25% sample during subsequent cooling is considered to be due to a change in conformational structure of the PEO which is evident from the disappearance of PEO (C) related peaks (i.e. 950, 1145, 1278, 1359, 1465 cm^{-1}) in the samples after heating. The disappearance of these peaks suggested that crystalline PEO melts during heating and a new structure involving PEO and ethylene glycol chains was produced. As the conformational changes in a polymer dissolved in a solvent can also result in formation of gel phase [15], the gel formation shown by 25% Pluronic in ethylene glycol can thus be caused by this conformational change. The disappearance of the peaks at 950, 1145, 1278, 1359, 1465 cm^{-1} suggests that as the samples are heated, a change in the conformation of PEO present in the F-127 takes place and this changed conformation of PEO, during cooling, results in increased polymer – polymer entanglements near 50^0C for the 25% sample and causes it to form a clear gel. Because both PEO and ethylene glycol have strong hydrogen bonding tendencies, strong hydrogen bonding between the PEO chains and ethylene glycol as compared to hydrogen bonding between PPO and ethylene glycol resulting in increased polymer to polymer interaction (entanglements) which can also be a cause of this gel formation [16]. However, for concentrations lower than 25%, as fewer polymer chains are present, the entanglements are not sufficient to cause a gel formation so the gel is only formed above a critical concentration of 25%.

The gel phase formed by Pluronic in ethylene glycol is therefore different from the gels formed by Pluronic in water in that the Pluronic in water gels are considered crystalline in nature with the packing of micelles in the liquid crystalline state as the main cause of the gel formation whereas gel formed by Pluronic in ethylene glycol is amorphous and PEO conformation change could be the main contributing factor towards the gel formation as suggested by results obtained during this research. Also, aqueous Pluronic gels return to their initial state (i.e. clear solution) upon cooling whereas Pluronic F-127 in ethylene glycol samples did not returned to the initial state of a turbid mixture, rather a white wax like solid structure was achieved.

Cooling near to 25^0C resulted in formation of a white wax like solid structure in all the samples and this is attributed to the re-solidification of the Pluronic. Since the conformational structure of PEO has changed, the appearance of white, wax like solid state upon cooling back to near 25^0C can be considered as the re-solidification of the amorphous PPO along with the PEO with a changed conformational structure. The molecules of ethylene glycol become entrapped between the solidified PEO and PPO structures on a macro level with some of the PEO dissolved in ethylene glycol and/or present in the form of gel and thus a white wax like solid structure appears. Presence of all the peaks associated with ethylene glycol in the solid samples (i.e. after heating) is evidence of its presence in the samples. Also, the micrographs shown in Figure 4.c and 4.d clearly suggest the presence of a crystal structure which represents the re-solidification of Pluronic F-127.

Conclusions

Samples of Pluronic F-127 in ethylene glycol were investigated in order to observe gel formation for the purpose of achieving a gel to act as support material for the jetting of caprolactam. Results suggested that the samples do not form a gel upon heating and stay as liquid. However, a gel state was identified for the highest concentration (i.e. 25%) during cooling and this was thought to be due to change in the conformation of PEO chains. The results further suggest that although, a gel was not obtained at higher temperatures, if used for lower temperature build environments (i.e. 25^0C) the experimented compositions can provide a possible material to act as support which can be very easily removed due to its water solubility.

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