Effect of heat stabilizer content on the gel characteristic of the modified-recycled PET for 3D printing filament application

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Abstract. This research identified the type of gel in the modified-recycled poly (ethylene terephthalate) (modified-rPET) filament, with various content of heat stabilizer, Pentaerythritol tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate. The content of the heat stabilizer used in this study were 0, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 pph. Gel characteristics of the modified-rPET filament were characterized by using the hot stage microscopy technique. It was found that gels with heat stabilizer at 0-0.3 pph showed the unmelt-gel formation characteristic. On the other hand, the addition of heat stabilizer at 0.4-0.5 pph showed the formation of crosslinked-gel characteristic, this gel does not melt even if the temperature reached to the melting temperature. This gel affects the process-ability of 3D printing. Therefore, it becomes clogged at the nozzle of 3D printer. Furthermore, this research also determined the crosslinked-gel contents inside the modified-rPET filaments, with various content of heat stabilizer, by a solvent extraction technique. Using trifluoroacetic acid/dichloromethane blended solution, it was found that at increase of the heat stabilizer content, the higher the content of crosslinked gel were observed significantly.

1 Introduction

Nowadays, 3D printing technology is widely used in various industries. It has built up three-dimensional objects by adding up fusing materials layer-by-layer from computer-aided design (CAD) allows for the creation of highly complex shapes. It is fast in production and can also reduce production costs [1]. Printing system via polymer extrusion, is the commonly system used for 3D printers. Commonly used standard polymers for 3D printing filaments such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS). Moreover, there are also engineering polymers including polycarbonate (PC) polyamide (PA), polyethylene terephthalate glycol modified (PETG) and Poly (ethylene terephthalate) (PET) [2]. The advantage of PLA filament, which has a low shrinkage property which can print the high accuracy shape of specimen. But the weak point of PLA is low heat resistance, it cannot withstand temperatures over 60 ºC. Which means it cannot be used for outdoor applications. Meanwhile, ABS, PC, PA, PETG and PET are withstanding at higher temperature compared with PLA. But all of them have high shrinkage behavior, which is not suited to printing the high accuracy products as required from industrial application.

Because of these problems, our previous work has solved the shrinkage problem. The polymer used in our previous work was PET recycling from drink bottle waste (rPET). It was because PET has high temperature resistance, no toxic to humans while printing. Moreover, the recycling of PET is also friendly to the environment [3].

Normally, Poly (ethylene terephthalate) or PET has good mechanical properties, light weight, clear, and resistant to chemicals and gas permeability. It also could be processed by many processes, which could be produced into many products, especially drink bottled [4]. Consequently, there is a lot of waste from PET bottles around the world. Hence, needs to be recycled to reduce the global waste problem. However, producing 3D printing filament directly from rPET has its drawbacks. Because rPET was ground from PET bottle waste into a flake form (small piece) which make it has lower molecular chain compared with PET virgin. Besides, rPET is polyester polymers, which is sensitive to hydrolysis during the thermal process, causing polymer chain scission. Resulting in low melting strength [5]. Consequently, it cannot be formed into a large filament or large workpieces. Furthermore, PET also has a slow crystallization rate at normal temperatures, resulting in a high shrinkage value.

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For this reason, our previous work successfully increased the melting strength by modifying the structure of rPET into a long chain-branching structure. By adding various additives to the polymer. The modified-recycled polyethylene terephthalate is called "modified-rPET". Moreover, our previous work also reduces the shrinkage by adding inorganic nucleating agents, to increase the rate of crystal formation and crystallinity of polymer [3]. However, after successfully modified rPET to improve the melting strength and reduce shrinkage. But we still found another problem that needs to be solved. This problem is "some big gels inside the filament". Although the big gels are not all over the filament. But only a big gel still causes the problem when printing workpieces. Because it will clog at the nozzle, causing the machine to stop and disrupt the process of 3D printing [6].

Gels are three-dimensional, networked polymer structures, formed by crosslinking reactions. Gels are caused by many factors. Including gels that are contaminated from the impurity products, from the manufacturing process (the gel can avoiding by get rid of the impurity); gels that formed from polymers, that are not fully melted due to the high extrusion rate the so-called "un-melted gel"; gels formed by the interaction of chains due to polymers have too high molecular weight, the so-called "high entanglement gel"; gels formed by polymers that are highly oxidized, the so-called "highly oxidized gel"; and gels formed from polymers that have undergone oxidation or have had excessively high amounts of polymer additives added, which are called "crosslinked gels" [7, 8]. The type of gel that may clog inside the nozzle, is crosslinked gel, as this type of gel does not melt at their melting temperature. Crosslinked gels may be created by adding high amounts of polymer additives, such as molecular chain-extenders, antioxidant, or certain types of heat stabilizers [6].

From literature reviews, many researchers obviously reported that the Irganox®1010 is used as heat stabilizer or antioxident in our previous research. It inhibits the free radicals during thermal oxidation. However, it also acts as chain-extender. Because their chemical structure has four branches that have reactive sites at each chain end (hydroxy end group(-OH)). In consequence of there is an opportunity that the end group of each branch could be interacted with other PET chain end. Resulting in a crosslinking reaction and gel formation could occurred. [6, 9]

The aim of this research identified the type of gel and determined gel content of the modified-rPET filaments, with various content of Irganox®1010, by using hot stage microscopy technique and a solvent extraction technique.

2 Materials and method

2.1 Materials

PET flakes from drink and beverage bottles waste were purchased from Thai Plastic Recycle Group Company Limited. Multi-functional reactive polymers (or Chain extenders): Acrylic epoxy resin were supplied from Chemical Innovation Company Limited. Heat stabilizer (or antioxidant): Pentaerythritol tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate, M_w 1178 g/mol. Hindered amine light stabilizer (or primary antioxidant): Bis(2,2,6,6-tetramethyl-4-piperidyl) sebaceate, M_w 481 g/mol; and antioxidant (peroxide decomposer type) Tris (2,4-di-*tert*-butylphenyl) phosphite, M_w 646.9 g/mol. The antioxidants and stabilizers above were supplied from Merit Solution Company Limited. The solutions are Trifluoroacetic acid (TFA) and Dichloromethane (DCM).

2.2 Equipment

A ventilated oven (Memmert, UN750plus) was used to dry the flakes and modified-rPET compound pellets to reduce humidity. To prepare the modified-rPET compound amd modified-rPET filaments using a co-rotating twin screw extruder (XINDA, SHJ-200). A Hot-Stages Microscope (METTLER TOLEDO, HS82) was used to analyze the type of gels.

3 Experimental

3.1 Preparation of rPET flakes

4-8 mm. Flakes of rPET bottle waste were selected. Then, deplete moisture by drying for 16 hours in an oven at 80 °C. The rPET flakes should be dehydrated to prevent hydrolysis of PET dering the extrusion process.

3.2 Preparation of rPET Compounds

Dried rPET flakes were mixed chain extender, antioxidants, and heat stabilizer (Irganox®1010) as shown in Table 1. Afterwards, these formulas were compounded by co-rotating twin screw extruder with a twin rod die (2 mm. diameter each). The temperature profiles were 50-115-185-200-200 and 185 °C, respectively. Speed of the screw rotating was 80-100 rpm. The filaments was cooled under water and collected by a pulling machine. Afterwards, cut the compounds into pellets.

Table 1. The formulation of the modified-rPET with various content of heat stabilizer.

Formulation (modified-rPET)	Content		
	Elvaloy® PTW (pph)	Joncryl® ADR 4468 (pph)	Heat stabilizer (pph)
rPET-H-0	12.5	0.3	0
rPET-H-0.05	12.5	0.3	0.05
rPET-H-0.1	12.5	0.3	0.1
rPET-H-0.2	12.5	0.3	0.2
rPET-H-0.3	12.5	0.3	0.3
rPET-H-0.4	12.5	0.3	0.4
rPET-H-0.5	12.5	0.3	0.5

Remark: All formulas in the table above were added Antioxidants (0.1 pph and 0.2 pph).

3.3 Preparation of modified-rPET filaments

Dried the modified-rPET compounds for 16 hrs in an oven at 60 ºC. The compounds were mixed via filament extruder. The temperature profiles were 50-115-185-200-200 and 185 ºC, respectively. Speed of the screw rotating was 80-100 rpm. The filaments was cooled under water and collected by a 3D printing filament pulling machine. Control the diameter of the modified-rPET filament to size 1.65-1.75 mm.

3.4 Characterization

Hot-Stages Microscope (METTLER TOLEDO, HS82) was used to analyze the type of gels in modified-rPET filaments. The samples are classified based on size, color, and shape. The modified-rPET filaments are cut using a blade, cross sections 5-10 µm thick. The sample was initially heated to 30 ºC to final temperature of 300 ºC. The temperature was increased with a heating rate and cooled down to room temperature at the rate of heating and cooling of 10 ºC/min.

Investigating gel types (Gel content analysis) was determined by a solvent extraction technique. Samples from 1 g of modified-rPET filament were immersed and extracted via a refluxing Trifluoroacetic acid (TFA) and Dichloromethane (DCM) solvent at the proper temperature within 40 ºC for 24 h, with agitation.

4 Result and discussion

Fig. 1 shown the camera images of the modified-rPET filaments with various content of heat stabilizer (Irganox®1010). Fig.1(a-e) shown that the addition of heat stabilizer content at 0-0.3 pph, resulted in better control of the filament size than the addition of heat stabilizer content at 0.4 and 0.5 pph as shown in Fig.1 (f-g). It was due to the addition of high amounts of heat stabilizer. The chain end groups of the heat stabilizer reacted with the chain end groups of the PET, causing the formation of gel inside the filament [6]. From this result it makes poor process-ability, poor diameter control-ability and filament-stability not very good.

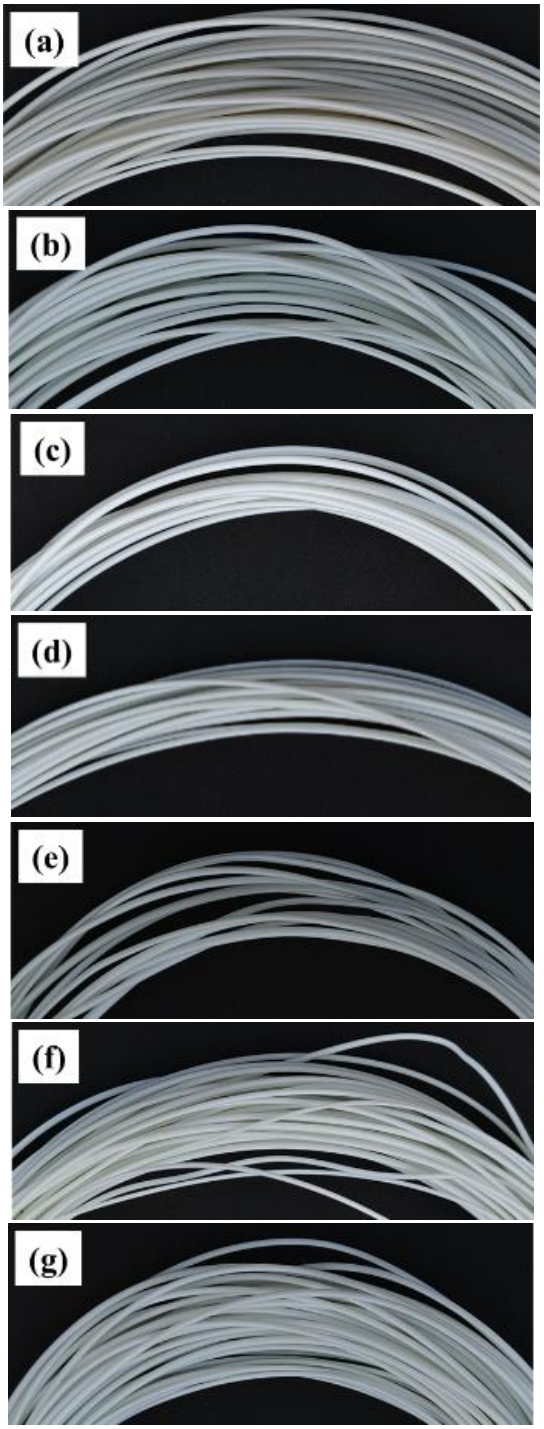

Fig. 1. Photograph images of the modified-rPET with the content of heat stabilizer at 0 pph (a) 0.05 pph (b) 0.1 pph (c) 0.2 pph (d) 0.3 pph (e) 0.4 pph (f) and 0.5 pph (g).

Table 2 shows the comparative summary results, including the process-ability, filament stability and diameter control-ability of the modified-rPET added with various content of heat stabilizer (0, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 pph). Furthermore, this result also compared with the filament of modified-rPET without antioxidants and heat stabilizer. These findings indicate that the optimal formulation, selected by the absence of gels, very good of process-ability and diameter control-ability, and high stability for continuous processing, is the modified-rPET filament containing 0.1 pph of heat stabilizer, referred to as “rPET-H-0.1”.

Table 2. The process-ability, filament stability and diameter control-ability of the modified-rPET.

Formulation (modified-rPET)	Content		
	Process-ability	Filament stability	Diameter control-ability
rPET-H-0	Good	High stability	Good
rPET-H-0.05	Good	Stable	Good
rPET-H-0.1	Very good	High stability	Very good
rPET-H-0.2	Very good	High stability	Very good
rPET-H-0.3	Good	Stable	Good
rPET-H-0.4	Medium	Stable	Medium
rPET-H-0.5	Poor	Not stable	Poor

Remark: The definition of the "Very good" and "High stability" are easy to control the size of modified-rPET filaments with heat stabilizer content has a diameter of 1.65-1.75 mm.

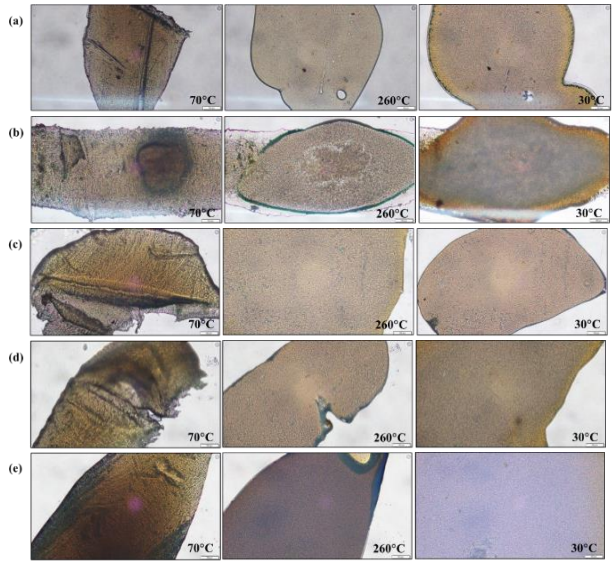

Fig. 2. Hot-stage microscopy images of modified-rPET filament with heat stabilizer at 0 pph (a) 0.05 pph (b) 0.1 pph (c) 0.2 pph (d) and 0.3 pph (e).

Fig. 2 (a-e) shown the hot-stage images of modified-rPET with heat stabilizer content at 0, 0.05, 0.1, 0.2 and 0.3 pph, it was showed an "unmelt-gel" formation charateristic. This was because when heated to melting temperature, the gel melted completely as showed the translucent image character.[7] And when the temperature decreased, it was found that the gel did not re-form, it still shows translucent character. The factor that caused this type of gel may be from the high extrusion rate during extrusion process.

Alternatively, Fig. 3 (f-g) shows hot-stage images of the modified-rPET filament with heat stabilizer content at 0.4 and 0.5 pph. They showed "crosslinked gel" formation characteristic. Because, when heated to the melting temperature range, the gel that forms in the filament does not melt (as show the dark spot at 260 ºC). [7] It was because the heat during this period being insufficient to break the covalent bonds. And when the polymer cooled down to the room temperature (30 ºC), the gel continued to re-form as show darker spot inside the images.

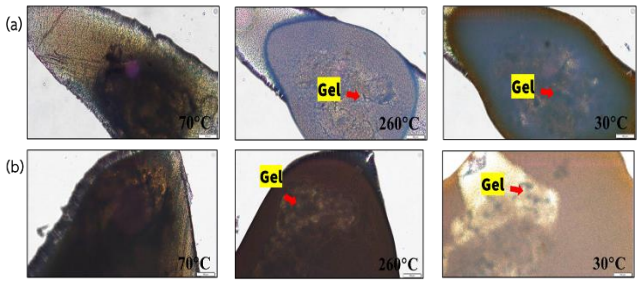

Fig. 3. Hot-stage microscopy images of modified-rPET filament with heat stabilizer at 0.4 pph (a) and 0.5 pph (b).

Table 3 shown the percentage of gel content (after a solvent extraction refulxing techinque) of the modified-rPET filament with and without heat stabilizer in various content. It was found that the formulation with 0.4 and 0.5 pph of heat stabilizer, had a high percentage of gel content compared with other formulations. However, with the highest content of heat stabilizer it has highest percentage of gel content, which is 75%. Whereas, when decreased the amount of heat stabilizer, the percentage of gel content decreased significantly. On the other hand, the gel content of the formula without heat stabilizer and the formular adding heat stabilizer at 0.05 pph, both formular has gel content higher than 0.1 pph. As a result of the gel could be formed by short chains of rPET and linked together into small groups until a gel forms, as shown in Table 3.

Gel content in the filament is not the only factor that can be a clogging problem. Moreover, size of gel inside the filament is also the main factor of the clogging problem. If the size of the gel that forms in the filaments larger than the nozzle diameter (0.4 mm), it will clog and affects the printing process. The size of the 3D printer nozzle that is commonly used is 0.4 mm as the standard. [10] Therefore, gels that are larger than 0.4 mm and are crosslinked gel will clog the nozzle and stop the machine.

Fig. 4 and 5 showed the gel size on filter papers which have been filtered images from the ImageJ program, to determine the size of the gel in modified-rPET filament with and without heat stabilizer. By

Table 3. The gel content (%) and average size of gel of the modified-rPET with various heat stabilizer content.

Formulation (modified-rPET)	Gel content (%)	Average size of gel (mm)
rPET-H-0	15	0.34
rPET-H-0.05	37	0.1
rPET-H-0.1	6	0.36
rPET-H-0.2	20	0.54
rPET-H-0.3	29	0.58
rPET-H-0.4	38	0.59
rPET-H-0.5	75	0.61

adjusting the image from the ImageJ program to find the gel area (opaque areas) from filter paper which has filtered from the polymer solution, dried the filter papers. And find the average size of the gel that does not pass the filter paper.

The gel size on filter papers as shown in Fig. 4 (a-c) which are the modified-rPET filament with heat stabilizer at 0 and 0.1 pph. It was found that the average size of the gel was smaller than the size of the standard nozzle. Which means although the gel content was high, this will not affect the printing process. The gel could be formed by the short chains of rPET reacting with added chemicals until the chains are linked together into small groups until a gel forms.

On the other hand, when the content of heat stabilizer increases (Fig 5, d-g). These formulations have a higher content of gel and show the large size of the gel also. This becomes a defect causing the nozzle to become clogged. Especially the formulations with added heat stabilizer at 0.4 and 0.5 pph, because it has "crosslinked gel" formation characteristic and the average size of the gel that forms in the filaments which is higher than that of a standard nozzle.

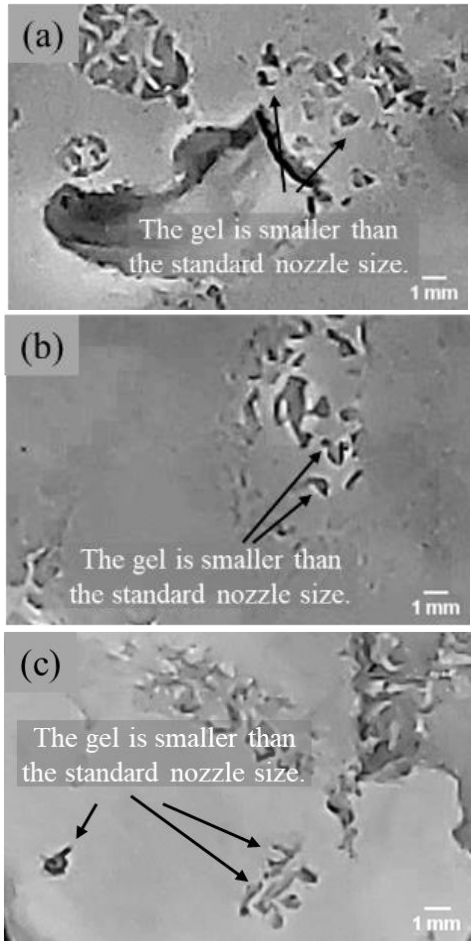

Fig. 4. Filter papers has been filtered images from the ImageJ program, to determine the size of the gel in (a-c) modified-rPET with heat stabilizer (0-0.1 pph) filament.

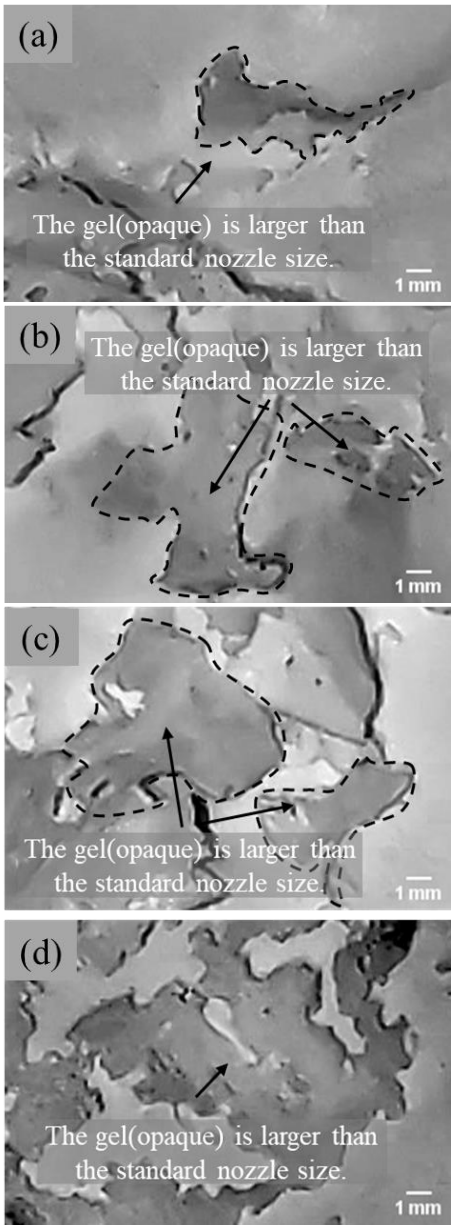

Fig. 5. Filter papers has been filtered images from the ImageJ program, to determine the size of the gel in (a-d) modified-rPET with heat stabilizer (0.2-0.5 pph) filament.

5 Summary

Identification of the type of gel and gel content formation in modified-rPET filament for 3D printing applications, it will reduce nozzle blockage and enable continuous printing. Make the workpiece have quality. This research identifies the type of gel that forms in modifed-rPET filament with various content of heat stabilizer. It was found that the most appropriate amount was the formulation of rPET1010-0.1 pph because it had good process-ability, stable filament stability, good diameter control-ability and only 6% of the gel formation. Focusing on a gel with unmelt-gel characteristics, which can be solved by increasing the extrusion rate within the production process. This type of gel will not block the nozzle. It is different from the crosslinked-gel characteristics which were found from the modified-rPET filament with heat stabilizer at 0.4

and 0.5 pph. This gel does not disappear even increases the temperature to melting point. Due to this temperature cannot break the bonds. Adding the higher amount of heat stabilizer affects the content of gel and the type of gel formed in the modified-rPET filament. Furthermore, it was also found that when the heat stabilizer was added over 0.1 pph, the average size of the gel formed in the filaments was larger than the size of a standard 3D printer nozzle. Consequently, to ensure accuracy in further analysis. Our future work, we will analyze the average molar mass and molecular weight distribution, to complete this clarification systematically.

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