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Interaction between Polyethylene and Petroleum Coke Substrate during Pyrolysis

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Abstract

There has been a constant growth for plastic demand globally in the past decades, and the continuing expanding trend with rapid emerging economies has increased the concerns of many parties. Various approaches of recycling waste plastic including chemical recycling, thermal recycling, and mechanical recycling has been practiced. As chemical recycling is known to be a promising method in recovering hydrocarbon compounds, which can be used in high-end product, new avenues for waste recycling need to be established. Consumable carbon anodes are a major requirement for process used for producing primary aluminum. Since carbon is a main constituent of waste plastics, which have very low impurity levels, these clearly have the potential as a cheap readily available auxiliary source of carbon in carbon anodes. Coal tar pitch, a major by-product produced in petroleum refining, is the binder of choice for carbon anodes. Pitch penetrates the pores of petroleum coke-binding particulates and gets carbonized during the baking process. In-depth wettability and interfacial phenomena investigation was carried out to study interactions between polyethylene (PE) and petroleum coke (PC). The effect pyrolysis parameters on degradation process of PE have been characterized. The wettability study of polyethylene polymer on PC substrates has been carried out.

Keywords: chemical recycling, waste plastic, heat treatment, pyrolysis, wettability

1. Introduction

Plastic industry has grown extensively in the past 30 years and is expected to grow steadily in future due to their product versatility. However, the relatively short life span of plastic goods has caused abundance of waste plastic globally where only 60 % of waste plastics are incinerated or buried into landfill. These methods have caused serious environmental problems and had led to the necessity of more efficient and novel recycling approaches that will not hurt

the environment at the effective cost. According to the statistic, waste plastic component only summed up to about 10 % of municipal solid waste (MSW), but due to its high volume to plastic ratio properties and also high resistance to chemical, weather, and harsh conditions, the amount of waste plastics piled up are worrying [1, 2]. Only 12 % of these waste plastic is incinerated while the remainder is end up to be landfilled. The waste landfilling method requires an active extraction industry, proper location that is close to waste generation, low cost transportation, and also must adhere to the policy requirements [3, 4]. The incineration of waste plastic will diminish the solid piled up, while recovering energy from the burning of waste but simultaneously emitting various environment pollutants [5].

Recycling plastic materials has become utmost serious business globally. There are variety of programs that were implemented to enhance the effectiveness of recycling and increase the awareness among consumers. Since plastics are mainly composed of hydrocarbon components, waste plastic are readily rich in carbon and have low impurity levels, which has the potential to be used as a cheap, abundantly available, auxiliary source of carbon. Owing to the high value of carbon in waste plastic, it can be used to produce consumable carbon anodes for industrial applications. Carbon anodes are manufactured by baking blends of some varieties of coke with hydrocarbon binder, which is generally a coal-tar pitch [6]. Prolonged treatment of waste plastic at high temperature (up to 1000 °C) has the potential of breaking down the hydrocarbon chain where the yield at the particular temperature and time can be used as a precursor for carbonization process for the anodes.

1.1. Recycling of waste plastic

Plastic is generally prepared from petroleum by-products and natural gas. These are composed of high molecular polymeric compounds containing primarily carbon, hydrogen, and a few other elements such as nitrogen and oxygen. Crude oil from petroleum is processed and refined to produce raw materials for plastics. Statistics have reported that total global plastic production has increased by an average of almost 10 % annually since 1950. The total plastic production has grown from around 1.5 million tons (MT) in 1950 to 322 MT in 2015 globally. China is the largest plastic producer, accounted up to quarter of world plastics, followed by Europe and former Soviet Union and North America [1]. Plastics have been one of the materials with the fastest growth because of their wide range of applications, but the duration of plastic life cycle is relatively small, which causes serious environmental problem every year.

There are three methods of recycling waste plastic that include material or mechanical recycling, thermal recycling, and chemical recycling. Chemical recycling or feedstock recycling allows the conversion of waste plastic into low molecular weight materials, which consist of their liquid or gaseous hydrocarbons for chemical industries. Chemical recycling can be classified into thermal decomposition, depolymerization (monomerization), and gasification (partial oxidation) [7]. Chemical recycling has been proposed as one of the most attractive methods for sustainable developments in the field. Waste plastics can be converted back into their original monomers or other valuable chemicals. Pyrolysis, one of the key chemical recycling techniques, has been used to produce a series of refined petrochemical products and particularly

liquid fractions similar to commercial gasoline [8]. Appropriate technique, including applied temperature and time of pyrolysis, is crucial in determining the desired polymeric product.

1.2. Pyrolysis of waste plastic

Pyrolysis as a process consists of chemical and thermal reactions, generally leading to the smaller molecules. Pyrolysis may be performed using a range of parameters such as temperature, reaction time, pressure, the presence or absence of reactive gases or liquids, and use of catalysts. Plastic pyrolysis can be conducted in three ranges of temperatures, which are low (<400 °C), medium (400–600 °C), and high (>600 °C). Pyrolysis temperature and heating time are known to enhance bond breaking and favor the production of smaller molecules while longer residence time increase the formation of secondary primary products, yielding more coke, tar, as well as thermally stable products, thus gradually obscuring the effect of original polymer structure. Pressure applied on the other hand determines the condensation rate of reactive fragments forming coke and heavy chain products.

Pyrolysis of two major plastics, PE and PP, has shown major conversion of plastic into oil with a low concentration of gas and no solid residue. The emitted hydrocarbon gases observed from the pyrolysis consist of alkane gases, methane, ethane, propane, and butane. Studies on the pyrolysis done at 430 °C of waste plastic mixtures have also been reported by Bhaskar et al. [9], describing the yield of liquid, gas, and residue from municipal waste plastic as being 59, 25, and 16 % weight, respectively. There is a significant level of liquid yield from pyrolysis; similar results have also been reported by Lee and Shin [2] in their pyrolysis experiments conducted at 350 °C and 400 °C. The liquid products obtained from the pyrolysis of waste plastics mainly consisted of liquid paraffin, liquid olefin, liquid naphthene, and liquid aromatics, with their relative proportions varying with polymer types, temperature, and lapse time. McIlveen-Wright et al. [10] have reported that the pyrolysis of waste plastic is important as it can provide oil and wax feedstock for the production of new plastics or refined fuels. The treatment can also generate a range of gases such as hydrogen, methane, ethane, and propane at higher temperatures. The main products are gas, oil/wax, and char products in some cases as its production depends on the types of plastic, reactor type, and process conditions [11].

2. Experiment

The research was focused on the polyethylene (PE) polymer as it is one of the mainstream waste plastic. PE was obtained from ExxonMobile Chemical. LL 6201 contains heat stabilizer, is high flow PE grades of 50 g/10 min melt-flow index (190 °C/2.16 kg) (based on ASTM D1238) with 0.926 g/cm³ density, and 123 °C melting temperature. PE has high calorific value of up to 80.30 % carbon, 19 % hydrogen, 0.03 % sulfur, and 0.52 % ash. **Figure 1** shows raw polyethylene samples used in the experiment.

Petroleum coke (PC) clumps was supplied by Rio Tinto Australia. Samples were then sieved to segregates for particular particle size for further analysis and then ground by ring mill into fine powder (**Figure 2**).

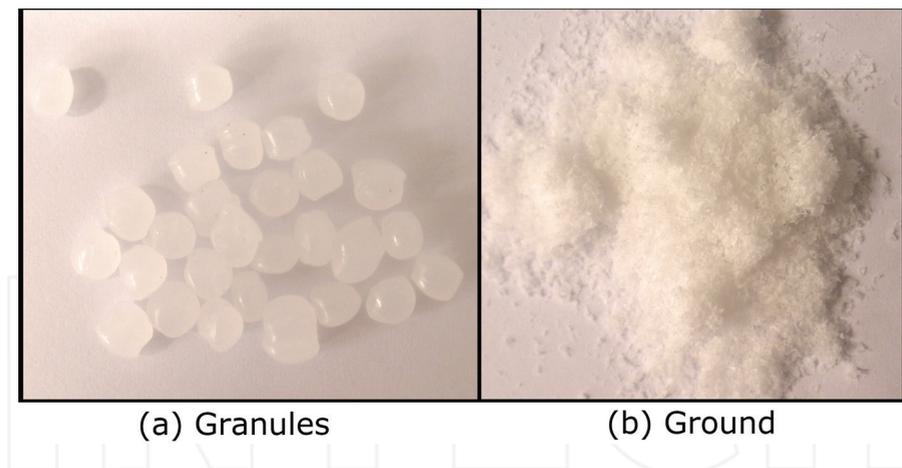


Figure 1. Raw polyethylene samples in (a) granules and (b) powder form.

2.1. Wettability studies

Petroleum coke powder were mixed with 5 wt% phenol formaldehyde binder and put onto roller milling machine for 24 h to ensure homogeneous mixing for preparing cylindrical substrates. The substrates sized 20 mm diameter and 5 mm thickness were prepared and baked at 180 °C for 24 h to carbonize the binder and harden the substrates. Small amount of ground polymer was put on the petroleum coke substrate and the assembly was charged into horizontal tube furnace under 1 L/min argon flow. Samples were then heated to 150, 200, 250, 300, and 350 °C and let soaked for 15, 30, and 60 min.

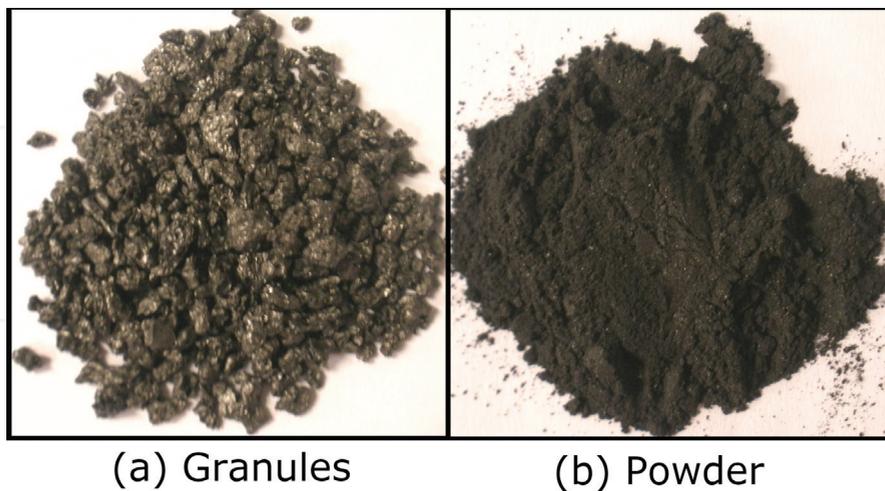


Figure 2. Raw petroleum coke samples in (a) granules and (b) powder form.

2.2. Heat treatment on the PE and PC mixtures

Ground PE and PC were weighted to obtain the desired weight percentages range from 10 to 50 %. The mixed samples were placed on roller milling machine for 24 h to obtain homogeneous mixtures. The mixture samples were placed in the tube furnace under purging of argon gas and undergoes three cycles of heat treatment as stated in **Table 1**.

Heating cycle	Baking method (1 L/min argon flow)
Cycle 1	Ambient temperature—heated to 150 °C and dwell for 30 min—cooled to room temperature
Cycle 2	Ambient temperature—heated to 150 °C and dwell for 30 min—heated up to 600 °C and dwell for 30 min—cooled to room temperature
Cycle 3	Ambient temperature—heated to 150 °C and dwell for 30 min—heated up to 600 °C and dwell for 30 min—heated up to 1000 °C—cooled to room temperature

Table 1. Heat treatment cycles method of polyethylene and petroleum coke mixtures.

3. Results

At 150 °C, PE starts to fuse together only after 30 min and liquefied after 60 min but no penetration occurs at this temperature. Similar observation was seen for up to 250 °C of heating where raw ground PE can still be seen, but as soaking time was increased to 60 min, the PE sample started to fuse together and adhere to the surface of petroleum coke substrate. PE has completely melted after 30 min of soaking at 300 °C where contact angle was calculated at 52.10 ° at this stage. However, the melt color still exhibited opaque raw PE. Prolonged soaking time to 60 min has decreased the contact angle between the melt PE and PC substrate to 36.30 °. The color of the PE melt started to change to translucent yellow at 350 °C, showing some bubble inside the melt. Increasing time has decreased the contact angle between PE and PC substrate (**Figure 3**).

This increment in the height becomes more obvious in samples treated at 300 °C. This increase may be due to the bubbles foaming from inside the PE melt. With the increasing temperature up to 300 °C, PE polymer starts to volatilize and starts releasing gases. The formation of bubbles was observed inside the PE melts from the SEM images. However, these bubbles formation are low and it may be due to the high viscosity nature of PE. The length of contact area increased significantly as the time was increased. These increasing lengths were due to the PE melt becoming less viscous which resulted in better spreading.

The mechanism of polyethylene degradation has been explained in a number of studies [12–14]. The degradation step is initiated by random scission reaction. Upon this reaction the polyethylene backbone may be further depolymerized by two competing reactions, e.g., (1) the propagation (unzipping) to yield monomers, and also (2) free radicals transfer which involves hydrogen transfer yielding the formation of unsaturated end and new free radicals [15].

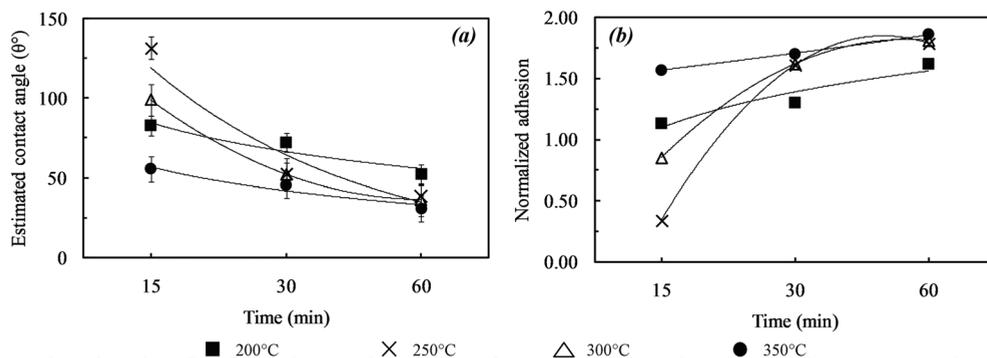


Figure 3. Effect of time and temperature on (a) estimated contact angle and (b) normalized adhesion of PE melt on PC substrate.

Temperature and residence time of the volatiles in the hot region of the furnace are the important parameters in determining the end-products of pyrolysis. This can be explained as the reaction products are produced from raw material decomposition, which is the primary reaction and also these primary volatiles product may be further depolymerized by secondary reactions that result in smaller monomers that mainly are in gases forms [15]. These primary reaction products are highly vulnerable to temperature and time of pyrolysis as they may undergo secondary reaction. Polyethylene is stable up to 290 °C but starts to reduce its molecular weight with increasing temperature. Polyethylene products varies according to the temperature where at mild degradation from 290 °C to 400 °C yield plastic similar to original polyethylene or hard waxes; and at extensive degradation results in semisolids pastes or liquids [16]. Pyrolysis of PE at 400–450 °C yields high liquid fraction of 69–84 and 9–13 wt% of gases [17, 18].

The weight loss of PE and PC sample mixtures undergoing heat treatment is plotted in **Figure 4**. The increase of PE ratio in the mixtures has decreased the percentage of residues obtained. The increasing of heat treatment temperature (Cycles 1–3) also lessens the weight of residues measured. This trend is expected as PE is composed of high volatiles that have been released during the heating cycles. Highest temperature of heating cycles (Cycle 3) results in the lowest residue left for both mixtures ratios, whereas the highest residues are obtained from Cycle 1, since at this temperature (150 °C) PE had not melted.

The effect of mixing and heat treatment cycles were also investigated by FTIR analysis. Each sample spectrum was stacked and compared in **Figures 5** and **6**, and the corresponding peak vibration has been characterized in **Table 2**.

The CH_2 stretching around 2913–2918 cm^{-1} shared by raw PC and raw PE is visible in all residues after the heat treatments. In contrast, another vibration of symmetric CH_2 at 2850 cm^{-1} in PE is lost after mixing with PC. The double bond stretching absorbed by raw PC (1685 cm^{-1}) also has been reduced after the mixing. Another alkene $\text{C}=\text{C}$ absorption, which is visible in PC and PE around 1645–1655 cm^{-1} , was intact throughout the heating cycles of up to 1000 °C (Cycle 3). Similar outcomes on the absorption of CH_3 bending (1457–1459 cm^{-1}) and $\text{C}=\text{CH}_3$ bending (1059–1072 cm^{-1}), which originated from their raw samples, also

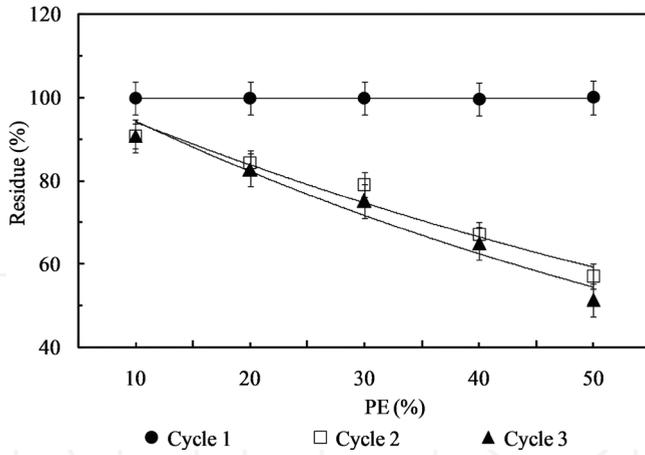


Figure 4. Residue left (%) of PE and PC mixtures after heat treatment cycles.

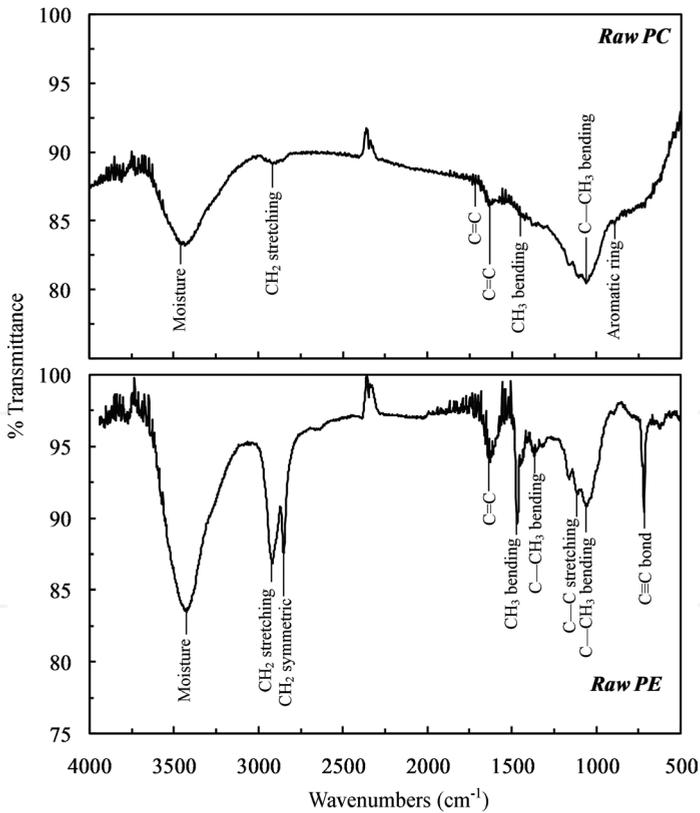


Figure 5. FTIR peaks of raw PE and PC.

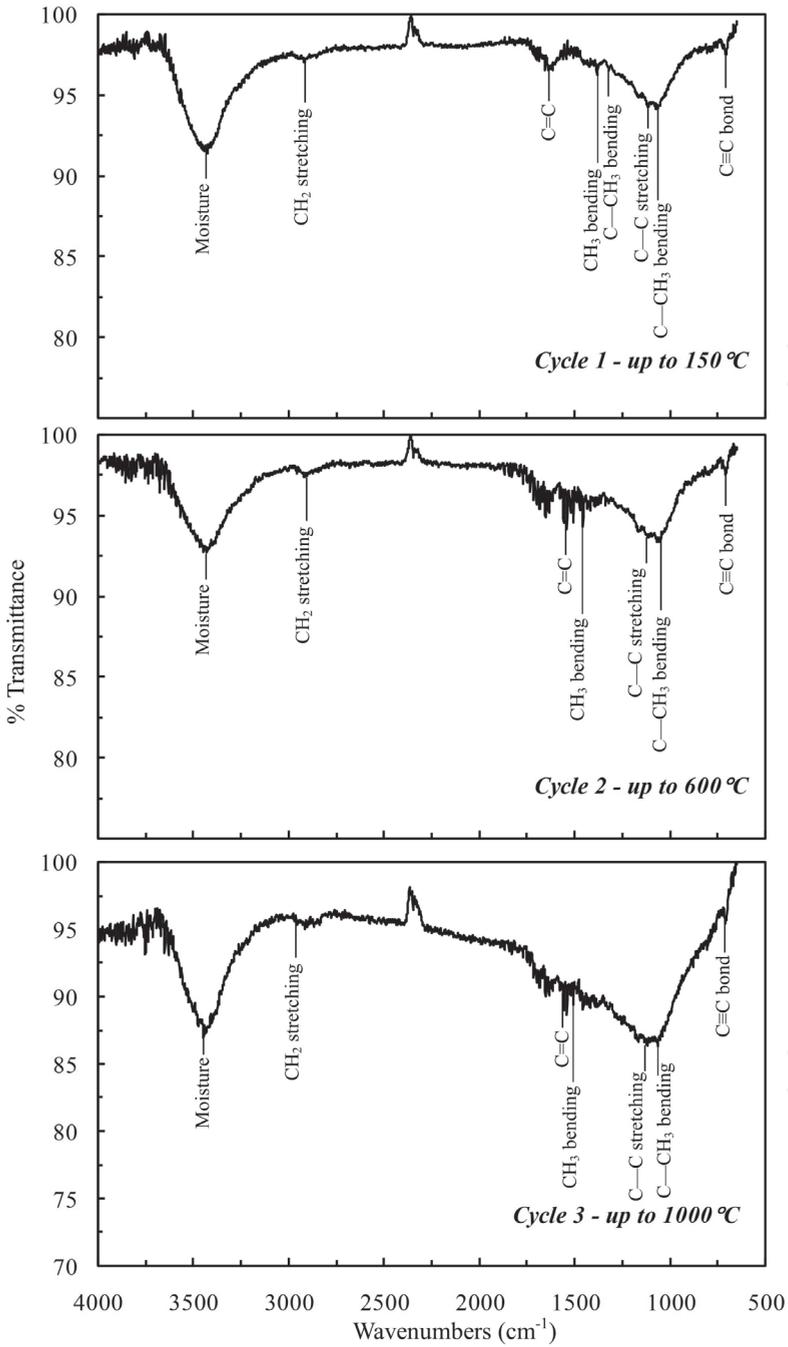


Figure 6. FTIR peaks of PE and PC mixtures at 50:50.

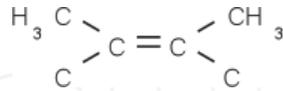
Raw PC	Raw PE	Cycle 1	Cycle 2	Cycle 3	Possible functional groups
3484.12	3477.22	3478.10	3489.31	3475.89	Moisture
2913.98	2917.98	2915.61	2918.56	2915.61	CH ₂ stretching
-	2850.54	-	-	-	CH ₂ symmetric
1685.49	-	-	-	-	C=C stretching
					
1653.83	1645.71	1651.96	1653.58	1653.37	C=C (alkene absorption)
1457.52	1459.20	1457.58	1457.67	1457.61	CH ₃ bending
-	1379.27	1383.55	-	-	C=CH ₃ bending
-	1162.30	1165.86	1168.48	1167.06	C=C stretching
1060.47	1059.33	1072.79	1069.93	1065.25	C=CH ₃ bending
893.93	-	-	-	-	Aromatic ring
-	718.30	711.80	708.86	708.86	Alkynes (triple C bond)

Table 2. Characterization of FTIR peak profiles of PE, PC, and their mixtures at 50:50.

survived in the heat treatment cycles. However, aromatic ring vibration at 893 cm⁻¹ from the raw PC has been significantly reduced after the mixture and heat treatment. Most of the peaks (raw PE) became significantly broader with reduced intensities after mixing and heating.

4. Summary

PE has a higher viscosity that limits its flow and penetration, where it has been shown that PE melted at high temperature, 250 °C after 60 min residence time. As mentioned earlier, PE has high viscosity that is influenced by temperature and time of the heat treatment. At the highest treatment parameters, of 350 °C temperature and 60 min time, PE melt has flattened on the substrate with contact angle of 30.90 °. The higher contact angle showed by PE was measured by its melt, without much disruption, while the bubbling and blistering of PE melt have caused it to increase the contact angle on the substrate surface.

The interaction behavior between PE and PC was further investigated by mixing PE in 10–50 % with PC and subjected the mixtures into heating cycle's heat treatment. The treatment of Cycle 1 (150 °C) has showed no changes in mass loss, whereas heating of Cycle 2 (600 °C) has showed some traces of PE, where the percentage of loss is about 33 and 43 % in 40 and 50 % PE mixtures, respectively. However, high temperature heating of Cycle 3 (up to 1000 °C) has totally decomposed PE in the mixtures. This result is in agreement with SEM images where the EDS analysis detected the presence of PE until Cycle 2 (600 °C) and was absent after Cycle 3. The carbon

content of the mixtures residues was in the range of 92–97 %, with the decreasing value with increasing time and temperature.

The residues of 50 % PE blend were also analyzed by FTIR to investigate the effect of blend, temperature, and time on the chemicals' bonding of its residues. PE is composed of many functional groups, some of which were reduced in intensity and became broad with increasing time and temperature. The CH_2 symmetric vibration at 2850 cm^{-1} was gone after the mixture, whereas $\text{C}-\text{CH}_3$ vibration around 1380 cm^{-1} was lost after Cycle 2. The reduced intensities and broader peak occurred after the heat treatment indicates that the temperature has decomposed those functional groups, and they gradually disappeared after progressive heating.

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