

Wettability and Interfacial Phenomena Investigations on High-Density Polyethylene and Petroleum Coke

Sharifah Shahnaz,¹ Rita Khanna,¹ Kamarudin Hussin,² Veena Sahajwalla¹

¹Centre for Sustainable Materials Research and Technology, School of Materials Science and Engineering, University of New South Wales, Sydney, NSW2052, Australia

²Universiti Malaysia Perlis, Jejawi, Perlis, Malaysia

Received 4 April 2011; accepted 29 September 2011

DOI 10.1002/app.36284

Published online 19 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: An in-depth wettability and interfacial phenomena investigation was carried out to study interactions between high density polyethylene (HDPE) and petroleum coke. The aim is to investigate the effect of temperature and contact times on possible interactions and adhesion characteristics for partially substituting coal-tar pitch binder with waste polymers. Using a sessile drop arrangement, experimental assemblies consisting of ground HDPE and a petroleum coke substrate were heat treated in the temperature range of 150–350°C for 15–60 min. Contact angles between molten HDPE and petroleum coke surface and depth of penetration of HDPE into petroleum coke substrate were measured. The highest contact angle (131.5°) was observed at 250°C after 15 min. and lowest contact angle

(30.9°) was observed at 350°C after 60 min. Highest penetration depth (75 μm) was observed at 350°C after 60 min and lowest penetration (13 μm) at 200°C after 15 min. Analysis of results showed that increasing time and temperature of heat treatment had a significant impact on the interactions of molten HDPE with petroleum coke. Longer residence time and higher temperatures increased the extent of melting of HDPE, which in turn resulted in improved wettability and deeper penetration into petroleum coke substrate. HDPE was found to bind and adhere strongly with petroleum coke. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2056–2062, 2012

Key words: high density polyethylene (HDPE); petroleum coke; wettability; interfacial phenomena

INTRODUCTION

Plastics production and usage has grown significantly in the last 30 years and continued future growth is expected. Because of relatively short life spans of plastic goods, there has been a tremendous growth in the generation of plastic wastes. Post-consumer plastic wastes are projected to increase to 30 million tonnes in the USA alone with the worldwide waste generation levels being much higher.¹ Although the waste plastic component in municipal solid waste (MSW) amounts to ~10%, plastics have high volume to weight ratio and are generally not biodegradable. A number of techniques have been developed to recycle waste polymers including thermochemical conversion to energy dense fuels via gasification processes.^{2–4} European initiatives use waste plastics to create energy in conventional incinerators, cement kilns, and to produce heavy oil by pyrolysis. A 'Thermoselect Process' was developed in which dioxin and furan emissions were significantly reduced through rapid cooling of off-gases.⁵ Two companies in Japan (JFE and Nippon Steel) and one in Germany (Bremen

Steel Works) are currently using waste plastics as a fuel source in blast furnace ironmaking.⁶ It has been suggested that the simultaneous injection of waste plastics with coal in an innovative oxygen Blast Furnace could provide up to 25% reduction of greenhouse gas emissions.⁷ In Australia, the author's group has successfully utilized waste polymers as a carbon and energy resource in electric arc furnace steelmaking.⁸

Coal-tar pitch is added to petroleum coke to primarily act as a binder; it is also known to enhance the coking properties of coals and quality of resulting cokes as pitch can act as a hydrogen donor at high temperatures.^{9,10} Some macromolecules such as unsaturated polymer resins were found to reduce the carcinogenic content in pitch.^{11,12} The co-coking of coal with synthetic polymers was not successful because thermoplastics decomposed below the plastic temperature range of coals.¹³ In addition most elastomers and thermosets could not be liquefied at all. Therefore, synthetic polymers were first converted by liquid-phase thermolysis with coal-tar pitch, which yielded reaction pitches (RP) that were then used as reactive additives in co-coking of coal.¹⁴ Min et al. have developed a co-coking process of coal with waste plastics wherein the plastics were converted to coke, tar, light oil, and gas.¹⁵ This study has reported that the addition of polymers in

Correspondence to: R. Khanna (ritakhanna@unsw.edu.au).

co-coking of coal tar pitch increased the carbonization yield by 3–5% and also impacted the optical properties of resultant coke.¹⁶

In this article, we report an in-depth wettability and interfacial phenomena investigation on interactions of high density polyethylene (HDPE) with petroleum coke in the temperature range from 150 to 350°C in an inert atmosphere. During pyrolysis, HDPE is known to decompose into a solid residue, liquid, and gaseous products.¹⁷ Presently very little is known regarding the wettability and adhesion tendency, if any, of HDPE with coke particles. This article is organized as follows: experimental details including the furnace design, reaction conditions, and techniques used to determine contact angles have been detailed in the following section. Experimental results and discussion on contact angles are presented as a function of heating temperature and time. Electron microscopic results have also been provided on the depth of penetration for a wide range of temperatures and time. These are followed by conclusions on the use of HDPE as a possible binder material for petroleum coke.

EXPERIMENTAL

Experiments were carried out in the following stages. The first stage involved the preparation of petroleum coke substrates prior to their heat treatment and interactions with HDPE. Petroleum coke clumps were milled using RockLabs Ring Mill into a fine powder (~200 μm). The petroleum coke powder was mixed with 5% phenol formaldehyde binder and rolled over the milling machine for 24 h to ensure homogeneous mixing. Totally, 1.5 g of mixed sample was then weighed and pressed in a mould under 8 kN of force Enerpac 10 Tonne Model PEMA1321 hydraulic pressing machine to pressures of ~4 MPa to make substrates. The pressures used were minimal and essential to prepare good quality substrates; same pressing procedure and pressures were followed for all substrates to minimise possible differences in porosity if any. Substrates were cured at 150°C for 24 h. The ground HDPE was supplied by Qenos Pty, which comes in white powder form with a purity of 98%. It has a melting point of 120–135°C and density around 0.930–0.970 g/cm³.

A schematic diagram of horizontal tube furnace used in this investigation is shown in Figure 1(a). The furnace was heated to the desired temperature and was continuously purged with Argon gas at 1 L/min. Figure 1(b) shows the assembly of petroleum coke substrate and approximate amount of HDPE powder placed on top of the substrate surface. The heat treatment was carried out in the temperature range 150 to 350°C with reaction times of 15, 30, and 60 min at each testing temperature. The reaction

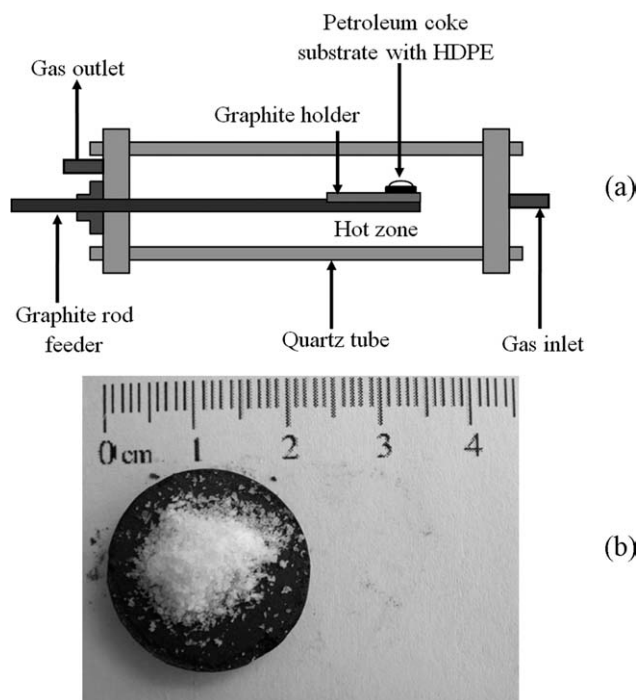


Figure 1 (a) A schematic diagram of horizontal tube furnace for sessile drop studies, (b) experimental assembly of HDPE atop a petroleum coke substrate prior to heat treatment.

assembly (petroleum coke substrate with HDPE on the top) was put into the furnace and held for the required time, before taking out and cooling down to room temperature in a desiccator.

The heat-treated sample was then mounted into the resin and dissected in half to expose the cross-sectional region. Samples were polished and coated with gold sputter for scanning electron microscopy (SEM) investigations. Measurements of contact angle and depth of penetration of the molten HDPE were carried out with the help of Photoshop CS5 software on SEM micrograph images. The techniques used for the measurement of contact angle and depth of penetration of the HDPE melt on the petroleum coke are shown in Figure 2. Depth of penetration was determined by measuring the distance up to which of HDPE melt had gone through the petroleum coke particles. The measurements were made on at least three sets of samples; mean values have been reported in this article. Results quoted in this article were within an error bar of ±5%.

RESULTS AND DISCUSSION

Wettability investigations

At 150°C, HDPE just started to melt and did not show any penetration into the petroleum coke substrate. After 15 min of heating, the HDPE particles were still found to be distinct and were well

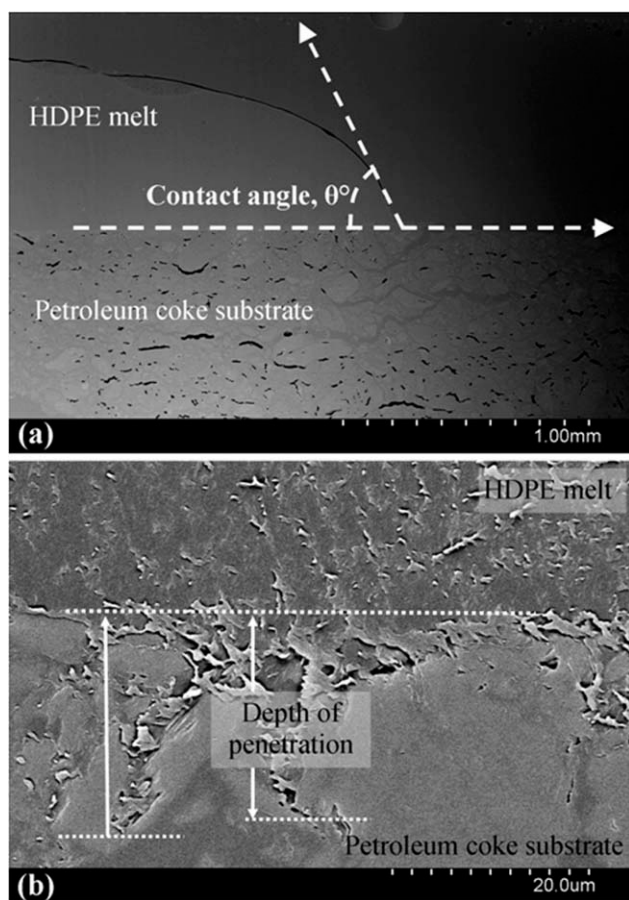


Figure 2 Experimental approach used to determine (a) contact angles and (b) depth of penetration.

separated; however, these started to fuse together when the time was increased to 30 min. As time was further increased to 60 min, HDPE polymer started to soften. No wetting or penetration was observed at this stage. After heat treatment at 200°C, HDPE was only partially melted even after 30 min. The color of HDPE melt was quite similar to that observed for the raw specimen. The SEM micrographs also showed that HDPE was not fully molten at this stage. After 60 min, the color of HDPE melt changed and became dense and opaque. The particulate form disappeared to a great extent; few spherical granulated raw HDPE bits were still visible from the top of the melt. HDPE melt had started to penetrate into the petroleum coke surface. Small voids noted in the samples heated for 15 and 30 min samples were no longer observed, but one large cavity that may have been produced due to some entrapment of gas inside HDPE particulate was observed.

The effect of heating at 250°C for 15 min was similar to that observed in the sample heated for the same duration at 200°C. These results have been presented in Figure 3 as a representative example. The HDPE did not melt completely as the particulate shape of the raw material could still be seen [Fig. 3(a)]. The solidified HDPE could be easily removed off the substrate. SEM image showed an uneven surface of the HDPE top region with high contact angles; large voids were observed showing unmelted HDPE granules within. The granular form of the raw HDPE was still recognizable after 30 min

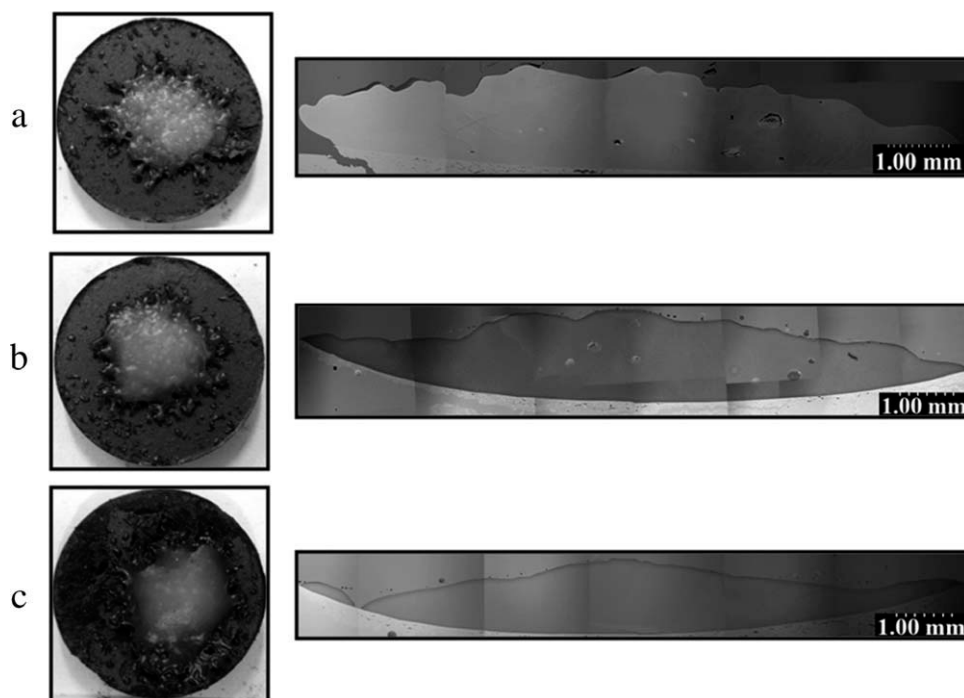


Figure 3 Experimental assembly after heat treatment at 250°C after a range of heating times. (a) 15 min, (b) 30 min, (c) 60 min.

of heating; however, it was more fused together as compared to the sample after 15 min of reaction. Longer time had allowed HDPE to melt further resulting in the dissolution of initial granular shapes. Lower magnitudes of contact angles indicate that HDPE melt had become more fluid after 30 min of treatment, leading to a better spreading [Fig. 3(b)]. After 60 min of exposure, the particulate shapes of the original raw HDPE were not observed anymore. However, some small bubbles were detected inside the HDPE melt. The contraction of HDPE on solidification caused the lifting of the upper layer of petroleum coke [Fig. 3(c)], thereby indicating a significant level of binding between petroleum coke and HDPE.

The heating of specimen at 300°C for 15 min also showed incomplete melting of HDPE with a high contact angle. However, increasing time to 30 min resulted in a complete melting of HDPE and decreasing contact angles. Some bubbles were observed inside the HDPE melt due to gas entrapment as melting progressed. The melt color was still opaque, exhibiting the color of raw HDPE. SEM images showed lesser number of voids and a smoother surface for the HDPE polymer phase. Molten HDPE was seen to penetrate into the petroleum coke surface and tended to form curved boundaries at the interface. After 60 min, HDPE had fully melted and the color of the melt appeared to be more translucent and glossy. Some bubbles were still spotted inside the melt. The melt had become less viscous and was spread on the substrate. The contact angle had reduced significantly compared with the samples exposed for 15 min and 30 min. Only a few small voids were observed in SEM micrographs.

When the samples were heated to 350°C for 15 min, HDPE had changed its color to translucent yellow. Several small bubbles were clearly seen inside the polymer melt. The increment in the heating time to 30 min led to a significant reduction in contact angle as it could achieve a greater extent of melt formation with associated reduction in viscosity. More bubbles were noted on the top of the melt compared to the sample heated for 15 min. However, these small bubbles had disappeared when the heating time was increased to 60 min. The viscosity of the melt is expected to reduce with increasing time at high temperatures thereby reducing the capacity of melt to retain gas bubbles which had escaped from the melt phase after 60 min. SEM image showed that the HDPE had flattened onto the substrate surface. The polymer region revealed a smooth surface without any cracks or voids.

Depth of penetration

In the interfacial region after heating at 200°C, a distinct appearance of HDPE polymer and petroleum

coke particles with well-defined boundary lines were observed at 15 min. The polymer was seen to be clearly surrounding and penetrating the available gaps between the petroleum coke particles. The penetration depth was determined as 12.83 μm . After 30 min, the HDPE polymer/coke interface appeared to be fibrous. In addition, HDPE was seen to penetrate deeper into coke. The depth of penetration increased after 30 min to 17.70 μm . The penetration of the polymer into smaller openings was observed after 60 min of heat treatment. This is to be expected as longer times resulted in further softening/melting of solid HDPE particles and therefore HDPE melt had become less viscous increasing the depth of penetration slightly. SEM image shows that the HDPE has penetrated in the upper layer of the substrate.

The effect of heating at 250°C is presented in Figure 4 as a representative example. Similar to the behavior observed at 200°C, HDPE did not show much penetration during the first 15 min. At this time, due to incomplete melting, it was unable to penetrate the gaps between the coke particles [Fig. 4(a)]. HDPE/coke interface also appeared to be very smooth, with small voids scattered all over it. The interface became much rougher after 30 min [Fig. 4(b)]. Short strands were seen emerging from the surface of voids. Penetration was observed at several places, even though the penetration depth was quite shallow (average of 22.81 μm). The penetration depth increased as the time was increased to 60 min. The HDPE fluid became less viscous as the time was increased to 60 min due to increased time available for melting; it was seen to penetrate small gaps between the coke particles [Fig. 4(c)]. As seen from the SEM micrographs, the fibrous HDPE had seeped through small openings between the petroleum coke particles, and got entrapped during its solidification, creating cracks as seen in the magnified image (2.50 μm size).

A low penetration depth (17.16 μm) was seen after heating at 300°C for 15 min. This value was marginally higher compared to the corresponding penetration for same time at lower temperatures. These results indicate that regardless of temperature, 15 min was too short a time for HDPE to melt completely even at 300°C and to penetrate deeper as the liquid phase was still viscous at this stage. After 30 min, the penetration increased to 25.93 μm . Longer times permitted further melting and infiltration of HDPE through smaller gaps between the petroleum coke particles. When the time was increased to 60 min, HDPE had clearly penetrated much deeper to 33.24 μm .

The penetration was relatively high (24.90 μm) after heating at 350°C for 15 min, which is comparable to that seen after heating at 250°C for 30 min (25.93 μm). After 30 min, HDPE penetrated further

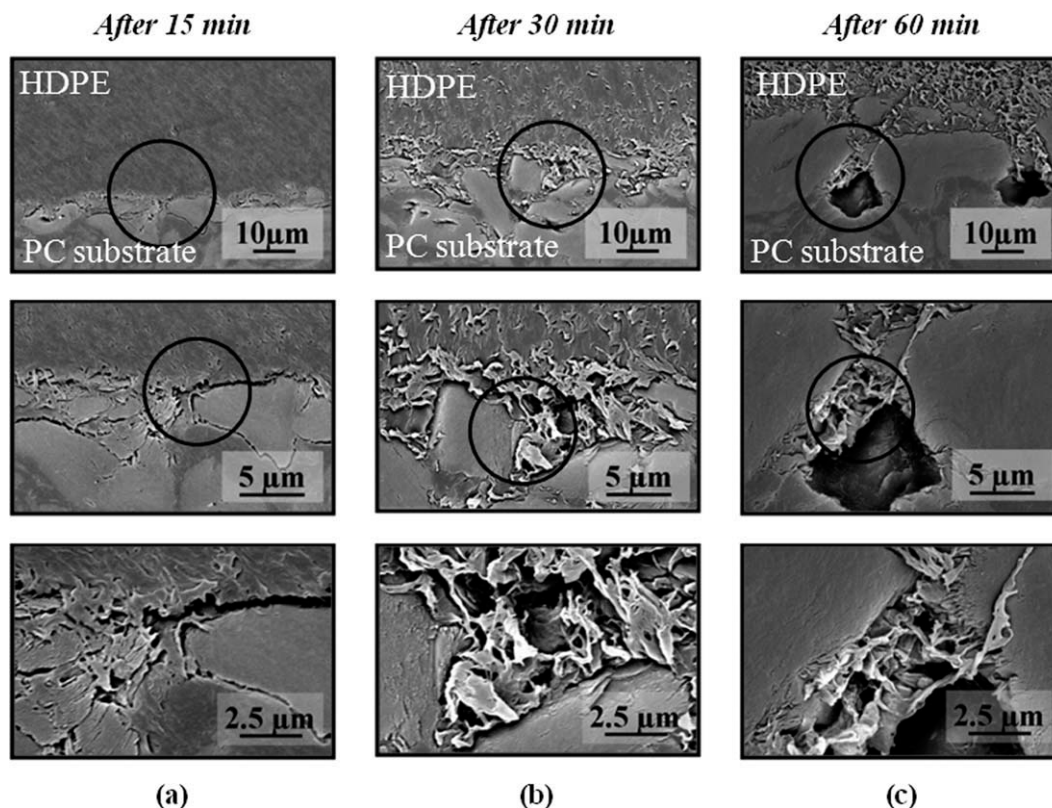


Figure 4 Interfacial region after heat treatment at 250°C after a range of heating times.

into petroleum coke substrate. The penetration and spreading of HDPE liquid through pores between petroleum coke particles were similar to the heat treatment at 300°C. The HDPE was seen sticking to the petroleum coke particles and was seen to penetrate through the cracks between petroleum coke particles.

Figure 5(a) summarizes the effect of time and temperature on the contact angles of HDPE on petroleum coke substrate. Contact angles were seen to decrease with increasing time; this was attributed to the increased fluidity of the polymer phase. Corresponding results for penetration depths have been summarized in Figure 5(b). The contact angle measurements showed that at 350°C, the contact angle did not change significantly after 30 min. These results are generally in good agreement with penetration depth measurements; a decrease in contact angles and improved wettability resulted in increased penetration depth of the polymer in petroleum coke matrix. A schematic of polymer penetration and spreading has been presented in Figure 6. The resolidification of the HDPE liquid after each of the heat treatment caused the surface of HDPE to contract. Some petroleum coke particles were also found trapped within the HDPE melt. Shrinkage of HDPE surface with solidification resulted in the detachment of the coke layer close to the interface. Deeper penetration also

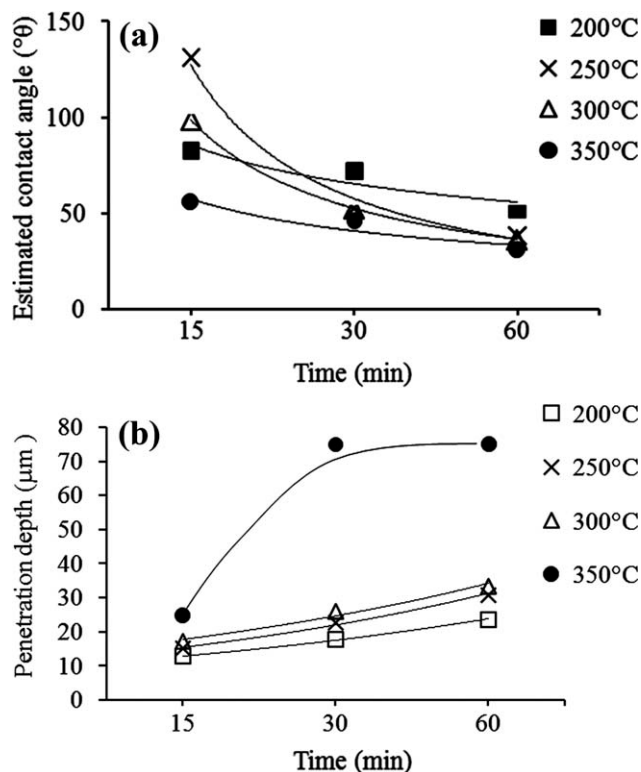


Figure 5 (a) Effect of time and temperature on (a) contact angles, (b) penetration depth for HDPE in contact with petroleum coke.

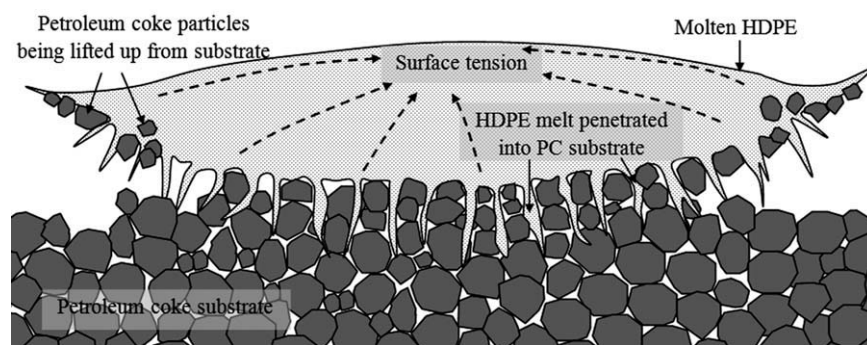


Figure 6 A schematic representation of mode of penetration of HDPE in petroleum coke substrate.

led to a greater binding of HDPE and coke particles from the substrate surface.

The degradation mechanism for polyethylene has previously been reported in literature.^{17–19} Thermal degradation is a process in which polymer melts at high temperatures and breaks down into smaller molecules. HDPE is a polyolefinic plastic, a difficult material to pyrolyze as it produces high viscosity products such as low-quality wax. HDPE begins to soften at a temperature as low as 150°C, but even after 60 min of heating it only softened to some extent. HDPE has a softening temperature around 101°C and expected to melt at 120°C.^{14,17} The initiation step involves a random scission reaction, which is generally followed by two competing reactions, e.g., the propagation (unzipping) to yield monomers, and free-radicals transfer which involves hydrogen transfer that results in the formation of unsaturated end, saturated end and new free radicals. The important aspects that need to be considered when determining the end-products of pyrolysis is the pyrolysis temperature and the residence time of volatiles in the hot zone of the reactor as the reaction products are formed from raw material decomposition (primary reaction) and as well as through the secondary reactions of the primary volatiles.

The pyrolysis products are very sensitive to temperature and time. Polyethylene is stable up to 290°C but its molecular weight starts to decrease with increasing temperature. The product of mild degradation (290–400°C) is a plastic similar to original polyethylene or hard waxes, while extensive degradation yields semi-solids pastes or liquids.¹⁹ Our experimental results are in good agreement with these findings. Gaseous volatiles (fumes) were observed in this study during the heat treatment at 300°C; however, the volume of gas produced visually appeared to be lower in those experiments where the penetration of molten HDPE into petroleum coke substrates were higher. In these cases, penetration could be occurring at a faster rate than the rate of volatile production by polymer degradation. In addition, the presence of coke can act as a

physical and thermal barrier to the release of volatiles from the penetrated polymer. However, this cannot be confirmed at this stage.

The viscosity of the liquid product from pyrolysis of HDPE also depends on the residence time, as longer time allows for additional breaking of carbon-carbon bonds, as exhibited by the breaking of thick liquid into a thinner liquid and gases (secondary reaction). The bubbles formed on top of the molten HDPE indicate the formation of gaseous products caused once again due to secondary reactions. The top of HDPE tended to heat up faster and decomposed into lower viscosity liquid and gases, whereas due the heat transfer limitations, HDPE inside the substrate can take longer time to liquefy.

This explains to some extent the enhanced penetration of molten HDPE with increasing temperature where there is also greater driving force for heat transfer. With increasing temperature, the HDPE became more fluid and was able to flow deeper through petroleum coke particles during the same time period, e. g. at 350°C after 30 min of treatment, much greater penetration depth was observed as compared to the sample heated at lower temperature. The relative stability and decomposition of HDPE is likely to be impacted by the length of the chain, as its stability is known to decrease with decreasing molecular weight and number of weak links present in the molecules. Oakes and Richards²⁰ have reported the initial rate of C–C breaking is affected by the temperature, where the number of bonds broken were 0.38×10^{-18} g/h at 305°C and 80×10^{-18} g/h at 360°C.

CONCLUSIONS

Temperature and time have been found to have a significant influence on the wettability and penetration behavior of HDPE into a petroleum coke substrate. Higher temperature allowed higher chain breaking rates, while longer residence time allowed enhanced levels of secondary reactions. Both conditions can

lead to chain breaking, which resulted in more fluid phase and therefore better wettability. This phenomenon enhanced the spreading of molten HDPE on the substrate surface and allowed the liquid to flow through between petroleum coke particles, and increased the depth of penetration into petroleum coke. The results obtained have shown that when wettability improves due to the lower interfacial tension, a greater depth of penetration is observed. Improved wetting is an indication that bonding between HDPE and petroleum coke is developing, and HDPE could serve as a possible binder material and partially substitute coal-tar pitch. Ongoing research in our laboratories is underway to establish an understanding of the nature of bonding between HDPE and petroleum coke.

References

1. Curlee, T. R.; Das, S. *US Environ Protect Agency, Pollution Tech Rev* 1991, 201, 14.
2. McIlveen-Wright, D. R.; Pinto, F.; Armesto, L.; Caballero, M. A.; Aznar, M. P.; Cabanillas, A.; Huang, Y.; Franco, C.; Gulyurtlu, I.; McMullan, J. T. *Fuel Processing Technol* 2006, 87, 793.
3. Williams, P. T.; Slaney E. *Resources Conserv Recycling* 2007, 51, 754.
4. Lee, K. H.; Shin, D. Y. *Waste Manage* 2007, 27, 168.
5. Auchter, J. M.; Jackel, M.; Sakuma, Y. *Chemical Economics Handbook-SRI International*, 1993.
6. Murai, R.; Asanuma, M.; Kashihara, Y., Sato, M.; Ariyama, T. *Australia Japan Iron and Steelmaking Symposium*, Sydney, Australia, 2004.
7. Sekine, Y.; Fukuda, K.; Kato, K.; Adachi, Y.; Matsuno, Y. *Int J Life Cycle Assess* 2009, 14, 122.
8. Sahajwalla, V.; Rahman, M.; Khanna, R.; Saha-Chaudhury, N.; O'Kane P.; Skidmore, C.; Knights D. *Steel Res Int* 2009, 80, 535.
9. Koehler, D. A.; Spengler, J. D. *J. Environ Manage* 2007, 85, 296.
10. Cheng, X.; Zha, Q.; Li, X.; Yang, X. *J. Fuel Process Technol* 2008, 89, 1436.
11. Zhibo, Z.; Nishio, S.; Moroika, Y., Ueno, A.; Ohkita, H.; Tochi-hara, Y.; Mizushima, T.; Kakuta, N. *Catalysis Today* 1996, 29, 303.
12. Collin, G.; Bujnowska, B. *Carbon* 1994, 32, 547.
13. Brzozowska, T.; Zieliński, J.; Machnikowski, J. *J Analyt Appl Pyrolysis* 1998, 48, 45.
14. Collin, G.; Bujnowska, B.; Polaczek, J. *Fuel Process Technol* 1997, 50, 179.
15. Min, Z.; Cai-hong, L.; Lei, M.; Xiao-Mei, W.; Zhi-Lei, Z. *Proceed Earth Planetary Sci* 2009, 1, 807.
16. Machnikowski, J.; Machnikowska, H.; Brzozowska, T.; Zieliński, J. *J Anal Appl Pyrolysis* 2002, 65, 147.
17. Wall, L. A.; Madorsky, S. L.; Brown, D. W.; Straus, S.; Simha, R. *J Am Chem Soc* 1954, 76, 3430.
18. Wampler, T. P. *J Anal Appl Pyrolysis* 1989, 15, 187.
19. Peterson, J. D.; Sergey, V.; Charles, A. W. *Macromol Chem Phys* 2001, 202, 775.
20. Oakes, W. G.; Richards, R. B. *J Chem Soc (Resumed)* 1949: 2929.