

Study on Dissolution of Low Density Polyethylene (LDPE)

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Abstract. The world is currently facing the problem brought by plastic waste, as well as energy crisis. It is known that catalytic cracking of low density polyethylene (LDPE) waste can produce liquid fuels with similar properties to fossil fuels, hence serve as a solution to the problems mentioned. However, the problem of pipelines clogging by molten plastic feed during the cracking process has to be solved before the process can be up-scaled to continuous process. It was proposed that LDPE waste can be dissolved in suitable solvent before being catalytically cracked under suitable conditions. Previously, a study was done to investigate on dissolution of virgin LDPE (in pellet form) and waste LDPE (in film form) in different solvents [1]. This study was done to investigate the behavior of virgin LDPE (in powder form) dissolved in several chosen solvents, namely benzene, toluene, chlorobenzene, isooctane, xylene and trichloroethylene, and compare the result with previous work. From the study, it was observed that LDPE samples could dissolve in benzene and toluene to a high extent. On the other hand, isooctane acted as a weak solvent towards LDPE powder. The difference of LDPE solubility in solvents was attributed to the surface area per unit mass of LDPE samples. Despite the superior property of benzene as solvent for LDPE, the safety factor study showed that toluene, xylene and trichloroethylene were more suitable to be used in LDPE dissolution. However, care should be taken to minimize possible effects of the solvents towards the body while using the solvents mentioned.

Introduction

There are many researchers who turned their attentions to pyrolysis of plastic waste, as it provides a viable solution to plastic waste recycling. Pyrolysis is a reaction where high temperature is applied to certain materials in the absence of oxygen, usually accompanied with high pressure. Under such condition, the materials decompose into smaller fragments, which may then recombine to form some other compounds. Extensive researches have been done by researchers on pyrolysis of plastic waste [2, 3] and municipal waste [4, 5]. However, before plastic waste pyrolysis can be industrialized, there are many obstacles that are yet to be solved, including the modification of pyrolysis from batch process to continuous process, which is commonly been applied in any other large scale process. In most researches, plastic waste is fed into the pyrolysis reactor in solid form, and then melted to form liquid at the temperature above 300 °C. Any temperature lower than plastic's melting point causes the solution to solidify. This can happen in the cases of process shut down or maintenance, causing blockage to the process pipelines. There is possibility of liquid feed to minimize coke formation during the process, but it has not been confirmed yet particularly for pyrolysis of plastic waste.

In order to overcome this problem, the dissolution/precipitation technique could be of great help. This technique is developed in the effort of recycling plastic waste. By using this method, plastic waste is dissolved in a suitable solvent to form solution, which is then comes in contact with a non-solvent. The dissolved plastic precipitates in the non-solvent are then extracted from the non-solvent through drying. The final product from this process is usually in granule form, with the quality similar to the virgin polymer. In addition, high recovery (~99%) can be achieved by using this technique [40]. One advantage of using this method in plastic recycling is its ability to separate the mixed plastic waste according to their difference in solubility and the use of different heating

temperature. This was shown in a pilot plant set up in 2001, which was used to separate and recycle plastic mixture of LDPE, as well as high density polyethylene (HDPE) and polypropylene (PP), by using xylene/propanol system. The waste was successfully recovered in lab scale with the use of solvent, anti-solvent and temperature. Further studies are required to investigate its possibility for up-scaling plastic recycling process [41].

Pyrolysis and dissolution/precipitation techniques are developed to serve the purpose of recycling plastic waste. However, the techniques can be modified to solve the problem of pipeline clogging during plastic waste pyrolysis. Plastic waste can be dissolved using heated solvent, and the solution formed is pyrolysed instead of being in contact with the non-solvent. The use of solution in the pipelines would cause no clogging even when the temperature is below the melting point of plastic. The solvent can be collected and recycled through drying process, hence reducing the materials cost.

In order to gain deeper understanding towards the pyrolysis of polymer waste dissolved in organic solvents, a study was performed to investigate the possibility of dissolving light density polyethylene (LDPE) in powder form in different solvents. Among the possible solvents, the best solvent to be used in LDPE dissolution was decided based on the dissolution time and its safety factor. Qualitative data were also obtained from this study, which is useful in the study of polymer degradation.

MATERIALS AND METHODOLOGY

Materials. Virgin LDPE polymer was purchased from Aldrich Company. Then, it was grounded and sieved to obtain powder in the range of 500 – 1,000 μm . Benzene, chlorobenzene, toluene, xylene, trichloroethylene, and isooctane solvents purchased were of analytical grade.

Methodology. Dissolution of LDPE powder in various solvents (i.e. benzene, chlorobenzene, toluene, xylene, isooctane, and trichloroethylene) was carried out at temperature of 85 $^{\circ}\text{C}$. For each solvent, the dissolution of LDPE sample was performed in 6 test tubes, each with different mass, and was labeled from A to F. The volume of each solvent used was kept constant at 5 mL.

During the experiment, the solvent was heated up to 85 $^{\circ}\text{C}$ before LDPE sample was added into the solvent. Times taken for LDPE samples to fully dissolve in each solvent were recorded. It was noted that the boiling point of trichloroethylene is 86.7 $^{\circ}\text{C}$, thus the temperature used for this solvent was controlled at 80 $^{\circ}\text{C}$ to avoid the boiling of solvent.

The experiment procedures above was performed for pure LDPE in pellets form (with diameter of $\sim 3\text{mm}$), as well as in powder form, and LDPE waste in sheets form. The data obtained were used to plot graphs, and the R^2 values of these data were found to be less than 0.97.

Result and Discussion

Dissolution of LDPE powder in solvents was observed to be similar to the previous study, where the LDPE powders swelled and turned from white color to colorless, before they dissolve in the solution. The mechanism of LDPE dissolution in the solvent was hence proposed. It was expected that when LDPE was put into compatible solvent, the molecules of the solvent were able to penetrate the surface layer of the polymer, and a swollen layer was formed between the solvent and the polymer layer. This process is termed as solvent diffusion. In this layer, solvent molecules were able to eventually break the bonding in the polymer at the outer swollen surface layer. As a result, LDPE molecules started to detach from the outer surface layer, and mixed homogeneously with the solvent molecules. This enables other solvent molecules to further penetrate into LDPE surface where LDPE molecules detached. This process continued until a quasi-stationary state is reached, where the molecules of the solvent were not able to penetrate the LDPE layer. This can happen when further increase of the layer is prevented by the transport macromolecules from LDPE to the solvent layer. For some solvents, their molecules are not able to penetrate the outer surface layer, or this happens very slowly, hence effective dissolution of LDPE in these solvents is hard to achieve. This mechanism is in accordance with the one proposed by Miller-Chou and Koenig [47], which discussed on the polymer dissolution in the solvent.

According to the results shown in Fig. 1, LDPE in powder form dissolved at faster rate in the solvents when compared to LDPE pellets [1], which has a diameter of ~3 mm. The dissolution of LDPE in solvents can be considered as a chemical reaction, hence as the size of a fixed amount of LDPE becomes smaller, the surface area of LDPE in contact with solvents becomes larger, and the dissolution mechanism proceeded faster. In this study, benzene was the best solvent used in dissolution of LDPE powder. It took only 2.35 minutes to dissolve 0.30 g of the powder. On the other hand, isooctane was able to dissolve 0.30 g of LDPE powder in 7.42 minutes, and it is the only non-aromatic solvent that can dissolve LDPE in this study. However, the dissolution rate was far slower than other solvent used.

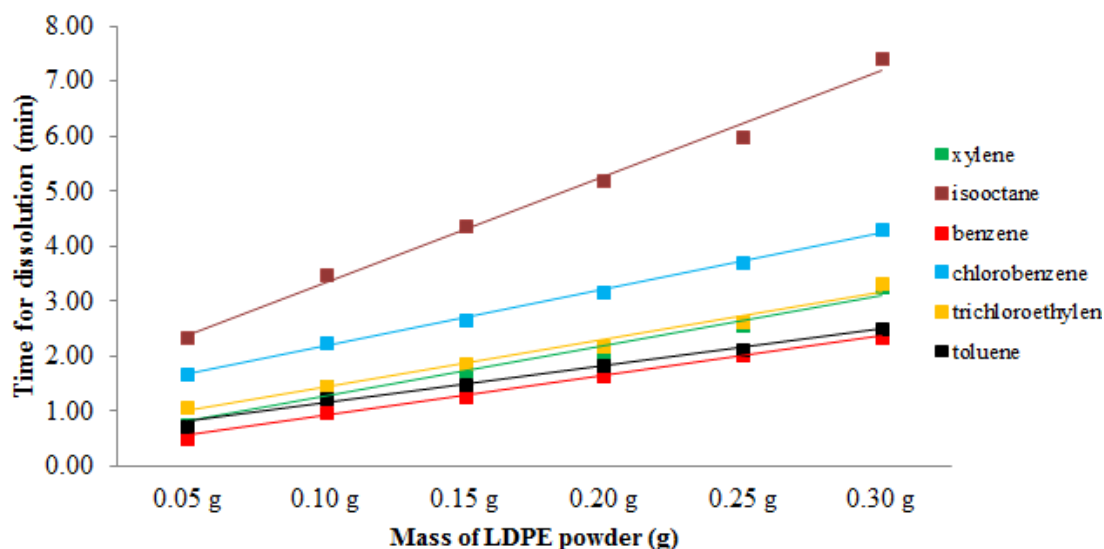


Fig. 1: Time needed for waste LDPE (in powder form) to dissolve in different solvents

Comparison of solvent to be used considering the aspect of safety. In order to decide the best solvent to be used for dissolution of LDPE, safety aspect of the solvent has to be considered. Materials Safety Data Sheet (MSDS) of the solvents used above have been studied, and several important data was summarized in Table 1 from Materials Safety Data Sheet obtained from the Science Lab Company.

According to the Hazardous Materials Identification System (HMIS) developed by American Coatings Association, almost all the solvents used in this study were classified in the same ratings for health and fire hazards, except for trichloroethylene, which obtained a rating of one in the flammability aspect. In term of their hazards, generally all of the solvents were hazardous. However, benzene and chlorobenzene were very hazardous in case of eye contact and skin contact respectively, while isooctane was classified as slightly hazardous material. Thus, it is less preferable to use benzene and chlorobenzene compared to other solvents. Therefore, xylene, toluene and trichloroethylene were acceptable to be used in LDPE dissolution, and suitable personnel protective equipment are required while handling them. Although isooctane is slightly safer, longer time to dissolve LDPE makes it less suitable to be used in real application.

Table 1: Safety data of solvents

Health Effects		Benzene	Chlorobenzene	Toluene	Xylene	Trichloroethylene	Isooctane
HMIS (USA)	Health	2	2	2	2	2	2
	Fire	3	3	3	3	1	3
	Reactivity	0	0	0	0	0	0
	Personal Protection	H	H	H	H	H	J
Chronic effects	carcinogenic	Yes	N.A.	Yes	Yes	Yes	N.A.
	Mutagenic	Yes	N.A.	N.A.	N.A.	N.A.	N.A.
	Tetratogenic	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Acute effects	skin contact	hazardous	very hazardous	hazardous	hazardous	hazardous	slightly hazardous
	eye contact	very hazardous	hazardous	hazardous	hazardous	hazardous	hazardous

Conclusion. Three types of LDPE samples, namely virgin LDPE, LDPE waste, and LDPE powder were dissolved in different solvents to determine the best solvent to be used for dissolution of LDPE. In all the experiments, benzene was found to be able to dissolve all types of LDPE samples in the shortest time when compared to other solvents. However, when considering the safety factor, hazardous properties of benzene makes it less suitable to be used in this application. Toluene, xylene and trichloroethylene were more preferable to be used, as they have similar performance to benzene, as well as less hazardous compared to benzene.

Further study will be carried out to investigate the suitability of LDPE in dissolved form in the pyrolysis process, as well as the possible products from the reaction.

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