Vietnam Journal of Chemistry, International Edition, **55**(5): 545-551, 2017
DOI: 10.15625/2525-2321.2017-00505

Effect of fly ash on mechanical properties and morphology of plasterboard based on recycled poly(ethylene terephthalate)

Thien An H Phung[1], Dong Quy Hoang[1], Bui Duy Du[2,3*]

[1] *University of Science, VNU-HCM*

[2] *Institute of Applied Material Science, Vietnam Academy of Science and Technology*

[3] *Graduate University of Science and Technology, Vietnam Academy of Science and Technology*

Received 15 August 2017; Accepted for publication 20 October 2017

Abstract

The purpose of this study was to synthesize plasterboard based on recycled poly(ethylene terephthalate) (PET) and fly ash. The molecular weight determination of unsaturated polyester (UP) from recycled PET was performed by functional titration method. The effect of initiator, benzoyl peroxide (BPO) on the curing kinetic of UP from recycled PET was studied by differential scanning calorimetry (DSC) and at 2 phr BPO led to good curing process. The content of fly ash (50, 100, 150, 200 phr) at 2007 nm in diameter was used and the effect of fly ash content on some properties such as flexural strength, vickers hardness, and impact strength of plasterboard was researched. Test results showed an increase in mechanical properties, especially at 150 and 175 phr filler amount. In addition, the morphology of plasterboard at different fly ash contents was characterized by scanning electron microscopy (SEM). Also, chemical resistance of plasterboard was evaluated from the weight change in different chemical environment.

Keywords. Unsaturated polyester, Recycled PET, Fly ash, Plasterboard.

1. INTRODUCTION

Plasterboard panels are industrial building components. They are made in factories by locking a thin layer of gypsum (hydrated calcium sulfate) and additives between two cardboard sheets to create thin panels. Plasterboard is often mixed with fiber (typically paper and/or fiberglass), plasticizer, foaming agent, finely ground gypsum crystal as an accelerator, ethylenediamine-tetraacetic acid, starch or other chelate as a retarder, various additives that may decrease mildew and increase fire resistance (fiberglass or vermiculite), wax emulsion or silanes for lower water absorption. This is then formed by sandwiching a core of wet gypsum between two sheets of heavy paper or fiberglass mats. Plasterboard sheets usually apply for ceiling and wallboard; however, it also has several weaknesses such as hydrophilic property (very easy to decompose as contacting to water or turn to yellow color in high moisture environment) and shrinkage property after long time usage. To find a new material that has similar applications but overcoming these disadvantage and reducing cost, in this research we aimed to prepared plasterboard by combining unsaturated polyester (UP) from recycled poly(ethylene terephthalate) (PET) and fly ash with some suitable substances for mass production plan in near future by bulk molding compound (BMC). Polymer concrete synthesized based on UP and various filling materials that were studied by many authors [1-6]. PET resins are the most widely used thermoplastic in variety of applications such as high strength fiber, films, soft drink bottles and food containers. The consumption of PET in the beverage industry is significant increase, and a large number of disposable PET bottles have been recycled for many reasons such as reducing solid waste problems and obtaining valuable products from waste thermoplastics. There are two ways to recycle PET bottles: physical method and chemical method [7]. As for physical method, it is convenient for mass production; however recycled PET is often degraded due to hydrolysis that may lead to the viscosity or molecular weight not enough for procedure. To qualify standard viscosity for recycling, recycled PET must be dried to ensure that the maximum humidity is about 0.02 % [8]. This is very difficult specificity in the weather that has a high humidity (about 80 %); furthermore, requirement energy for drying leads to high costs. For chemical method, there are a number of depolymerization reactions such as hydrolysis, methanolysis, glycolysis, and aminolysis to obtain oligomer or monomer [9]. This monomer then is reacted with maleic anhydride to form available products like unsaturated polyester [8, 10, 11], polyurethane [12], and diacrylate or dimethylacrylate. In this paper, glycolysis was used to synthesize UP, a popular thermosetting widely used in many applications.

Fly ash is one of the residues generated in combustion in a cement industry. In the past, fly ash was generally released into the atmosphere. However, recently a majority of fly ash is stored for recycling like supplement in concrete production. The utilization of fly ash may be a benefit to the economy and environment due to reducing waste material. Many authors have focused on researching polymer concrete using a variety of thermosetting (epoxy, UP, UP from recycled PET) incorporated with many types of filling materials like sand, fly ash, or recycled concrete aggregates. These researches provide significant necessary data given by below examples. Mohd Hariz Kamarudin et al [13] carried out the experiments and concluded that storage module increased when increasing the amount of fine aggregate in the same particle size and at the exact filling amount, the increase of storage module was inversely proportional to the size of filling material. In addition, Gonzalo Martinez Barrera and Witold Brostow [1] synthesized successfully polymer concrete with 30 % UP and 70 % filling material in different size. They concluded when the size of filling material decreased, the mechanical properties of polymer concrete increased. Saravana Raja Mohan K et al. did research by combining fly ash and coconut fiber in concrete composite [14]. However, the difference from conventional polymer concrete, production in BMC machine requires homogeneous powder filler that is the reason we focused to examine effects of fly ash on properties of plasterboard. In this study, we used very fine fly ash powder generated in combustion in the cement industry with the same extremely size. In addition, BMC technique is able to make sophisticated shaped products but this method has quite a lot of inconveniences, especially material is rapidly hardened in cylinder in a BMC machine if methyl ethyl ketone peroxide initiator was used because the temperature in the cylinder is too high and the material hardens at that high temperature. In this case, we studied curing kinetic of UP resins from recycled PET with benzoyl peroxide (BPO), an initiator at high temperature. Combination of recycled PET bottle with fly ash not only contributes to improving green environment but also makes low production cost. Also, plasterboard based on thermosetting that attempt to overcome the weak points of traditional material (hydrophilic and shrinkage property).

2. EXPERIMENTAL

2.1. Materials

Benzoyl peroxide (BPO) used as a free radical initiator was manufactured by Pergan The Peroxide Company. Maleic anhydride (AM) that reacted with the glycolytic PET oligomer was provided by Merck. Ethylene glycol (EG) used for the de-polymerization at molar ratio was from Merck. The styrene monomer used as a solvent and an agent to link the adjacent polyester molecular was supplied from Merck. The tamol-N used as a dispersing agent was from Ludwigshafen. The SM5512 used as a defoaming agent was from Dowcorning Toray. Cobalt naphthenate as a promoter was from Shanghai Yancui. Calcium carbonate used as mineral filler was manufactured from VNT7 Joint Stock Company. The fly ash used as mineral filler was from SCL VN.

2.2. Synthesis of Unsaturated Polyester (UP)

Recycled PET from soft drink bottle [2] was cleaned, cut into small pieces with 4 × 4 mm in size, and dried in vacuum cabinet drier at 90 ^{o}C. This recycled PET was treated with zinc acetate solution in 1 % concentration. EG was mixed with recycled PET in the proportion of one to two in weight. Glycolysis experiments were carried out in a 500 ml three-necked glass reactor, equipped with a thermometer, a stirrer, and a reflux condenser with a nitrogen inlet. The mixture was stirred and heat to 200 ^{o}C for 2 hours. After that, maleic anhydride was added to mixture (AM/PET = 49/62 in weight) and then the reaction refluxed for 4 hours. UP product was obtained. Styrene monomer which is about 40 % of the total resins weight was poured into UP after cooling down the temperature to 60-70 ^{o}C. Then this mixture was stirred homogeneously. The molecular weight of the product was determined by functional group titration method [4, 8-18].

2.3. Preparation of plasterboard

UP resin after synthesizing from recycled PET was mixed with styrene monomer at 60-70 ^{o}C. Then, the chemicals such as BPO, SM5512, tamol–N, fly ash, calcium carbonate, and cobalt naphthenate were successively added into the mixture (table 1). Next, this mixture was poured into an aluminum mold and placed in a heat compress machine with compressed about 1700 kgf at 85 ^{o}C for 20 minutes. Then, cured product was post-cured in oven-drier at 110 ^{o}C for 24 hours. Images of finished plasterboard were shown in figure 1.

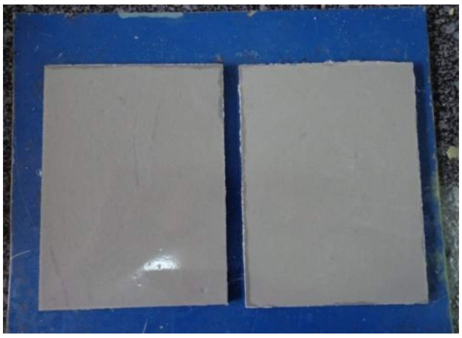

Figure 1: Images of plasterboard

Table 1: Ingredients in plasterboard

Ingredients	Content (phr)
UP from recycled PET	100
BPO	2
Cobalt naphthenate	0.6
SM5512	2
Tamol-N	5
Calcium carbonate	9
Fly ash	100, 125, 150, 175, 200

2.4. Characterization of plasterboard

2.4.1. Mechanical properties

Flexural modulus and flexural strength were performed on a universal testing machine AG-Xplus Shimadzu, Japan, according to the ASTM D790-00. Unnotched charpy impact strength test was performed on a Zwick HIT25P Shimadzu, Japan, according to the ISO179-1/1eU. HV hardness was performed on vickers hardness test method according to the ASTM C1327-08.

2.4.2. Morphological studies

The morphology of a cross-section of the fractured surfaces was examined by a JEOL JSM-IT100 scanning electron microscope (SEM- JEOL USA, Peabody, MA, USA) at an acceleration voltage of 5 kV. The specimens were sputter-coated with a conductive layer of platinum.

2.4.3. Chemical Resistance

The samples (50×10×3 mm^3) were dried in dry-oven until constant weight. The samples were immersed in different chemical environments such as HCl 30 % solution and NaOH 40 % solution for 2, 7, 14, and 28 days. Then these samples were dried in dry-oven and also were scaled definitely [3,6]. Weight change was calculated as follows:
Weight change (%) = $[(m - m_0)/m_0] \times 100\%$, where m_0: initial weight of samples, m: weight of samples after immersion.

3. RESULTS AND DISCUSSION

3.1. Determination of molecular weight

The molecular weight was identified by titration method. Glycolysis of PET and EG that obtained oligo-ester including hydroxyl group at end of molecular chain. The product was tested with acid (A) index and hydroxyl (B) index that were calculated in mg KOH/g by titration method. Then the molecular weight of oligo-ester was determined follows: $\overline{Mn} = (n \times 56.1 \times 1000) / (A+B)$ where n: the number of OH group in one molecular product (n = 2); A: acid index (mg KOH/g); B: hydroxyl index (mg KOH/g). The result of the molecular weight of the product was around 35000 g/mol.

3.2. Effect of catalyst on kinetic curing of UP from recycled PET

The thermal studies were made using a differential scanning calorimeter (DSC) from Mettler Toledo. The samples were precisely weighed and put into aluminum with a cover. The samples were heated from room temperature to 160 ^{o}C in the scanning mode with a heating rate of 10 ^{o}C/min in a nitrogen condition to obtain ΔH [18, 19]. The UP mixture after synthesizing was sampled to measure curing kinetic. The three quantities of BPO that cured unsaturated polyester from recycled PET were 1, 2, and 3 phr. The ratio of the catalytic of cobalt naphthenate was used at 0.6 phr.

Table 2: ΔH exothermal from DSC initiated by 1, 2, and 3 phr BPO

BPO (phr)	ΔH (J/g)
1	233.04
2	273.86
3	251.85

Figure 2 and table 2 show the heat released from the heated curing process with 1, 2, and 3 phr BPO. At 2 phr BPO, released heat acquired the maximum value with 273.86 J/g. This can be explained that two cross-linking mechanisms included inter-molecular and intra-molecular reactions that affected network formation [20]. Compare to 1 and 3 phr, at 2 phr BPO balanced inter-molecular and intra-molecular reactions that made curing process to achieve the best ΔH value.

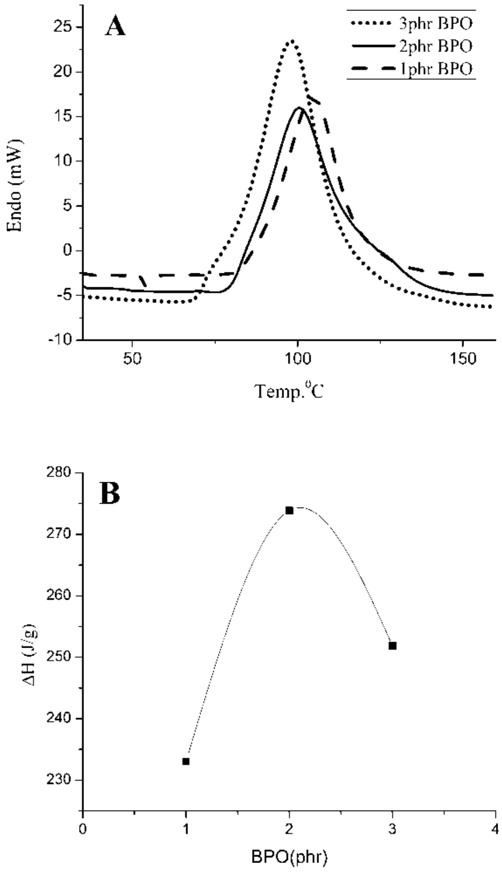

Figure 2: DSC cured of UP by BPO (A) and Heat curing value of UP by BPO (B)

3.3. Investigation of particle size of mineral filler

In this study, we aimed to make use of fly ash filling in the same size at different concentrations. However, the more increasing concentration of fly ash, the more increasing viscosity of the mixture, especially from 150 phr fly ash up, it is quite difficult to stir due to the homogeneous and fine size of fly ash (result in figure 3). To solve this problem, we co-operated dispersing agent (Tamol-N) and another filling material (calcium carbonate result of size in figure 4).

Dispersing agent (tamol-N) contains organic segments cooperate with inorganic segments that played an important role in increasing compatibility degree between organic phase (UP thermosetting from recycled PET) and inorganic phase (fly ash and calcium carbonate). In addition, calcium carbonate was used as mineral filler in order to disperse fly ash better in mixture due to different particle size. In this case, both calcium carbonate and fly ash have homogenous particles with 13620 nm and 2007 nm in diameter, respectively.

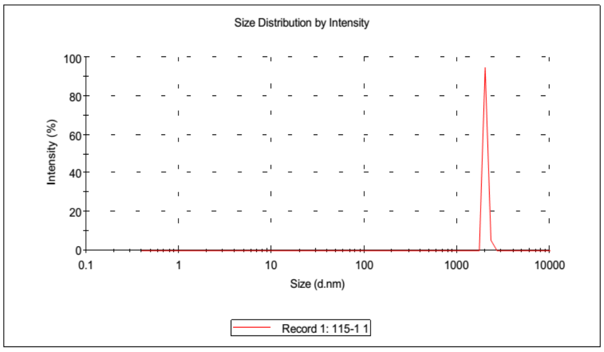

Figure 3: Particle size analysis of fly ash

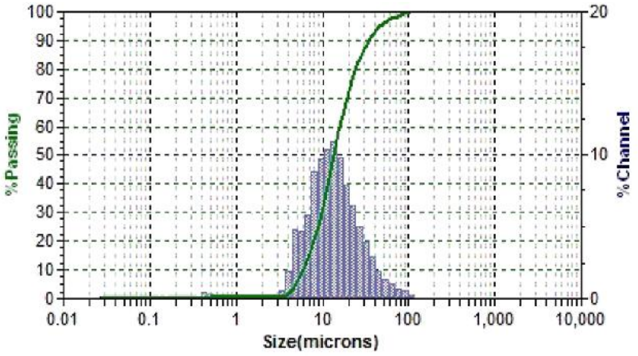

Figure 4: Particle size analysis of calcium carbonate

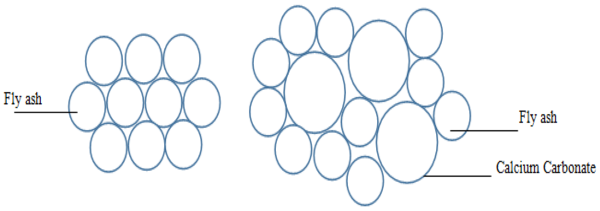

Figure 5: Model describes dispersion of fly ash with and without calcium carbonate

Figure 5 illustrated model where how different size filling materials were combined. Due to very small size, fly ash particles often precipitated, as a result calcium carbonate particles has higher diameter that reduced precipitation of fly ash.

3.4. Mechanical properties of plasterboard

As for the module and flexural strength, Figure 6 indicates when fly ash concentration increased, the value of module and flexural strength also went up, and reached a peak at 175 phr with module and the flexural strength were 12624.12 MPa and 49.63 MPa, respectively. This can be explained fly ash had a significant effect on plasterboard composite that helped to improve the flexural property, however when fly ash content was too much (200 phr) for UP thermosetting to cover all fly ash, the interaction between UP and fillers decrease, and these lead to decrease in value of the flexural property.

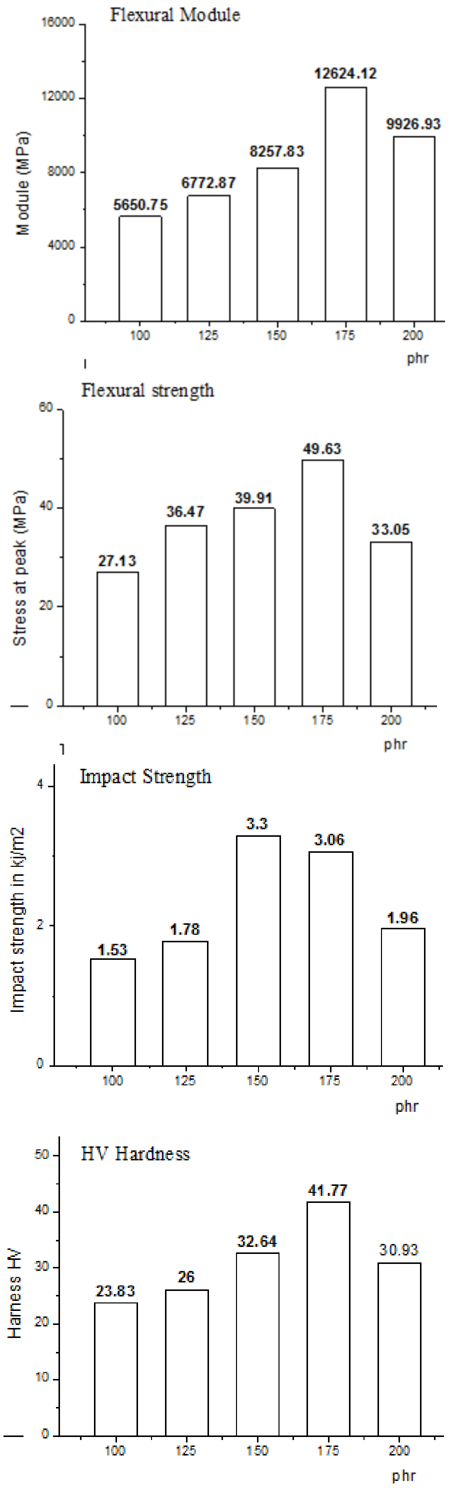

Figure 6: Mechanical properties of plasterboard in variety of fly ash concentrations

The result of hardness and impact strength also increase with the content of fly ash at 150-175 phr loading.

3.5. SEM micrographs

Figure 7 shows the microstructure of plasterboard composite with different concentration of fly ash at a magnification of 1000×. At 150 phr loading, the SEM picture showed smooth surface and no porosity present in the composite. For 175 phr loading, the surface had still smoothly although there were some rough places. However, at 200 phr loading, the picture shows a similar matrix with a few porosities in the surface, that indicate lower thermosetting weight was not enough to bond between filling materials. It was assumed that properties of plasterboard may be influenced by the presence of the porosity in UP matrix and it lacks adhesion [3].

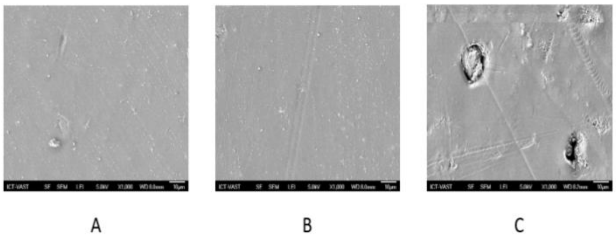

Figure 7: SEM of plasterboards in different concentration of fly ash (A: 150, B: 175, C: 200 phr)

3.6. Acid and base resistance

After immersing in 30 % HCl solution, plasterboard with 150-175 phr fly ash loading indicated the lowest changed values (0.1-0.2 %) whereas plasterboard with 100 and 200 phr fly ash loading caused a more significant change in values (0.5-0.6 %). Chemical resistance such as acid and base resistance have a key role in applications. The presence of fly ash increases the tightness, and as a consequence, that reduce the possibility of penetration of water and the chemical resistance. It can be seen from the figure 8B, after immersing in 40 % NaOH solution, plasterboard with 150-175 phr fly ash indicated the lowest changed values. At 200 phr fly ash loading, weight change accounted for 0.69 % and 0.68 % for 7 days and 14 days, respectively.

4. CONCLUSION

The recycling of PET waste through glycolysis was successfully performed. It is possible to reuse PET waste and fly ash waste materials in a valuable manner by synthesis new material such as plasterboard with the right for its commercial application. Effects of fly ash amounts on the mechanical properties and chemical resistance of plasterboard synthesized from recycled PET were studied and at 150-175 phr lead to increase in the flexural module and flexural strength. The morphology of plasterboards with 150-175 fly ash amounts showed smooth surface and no porosity.

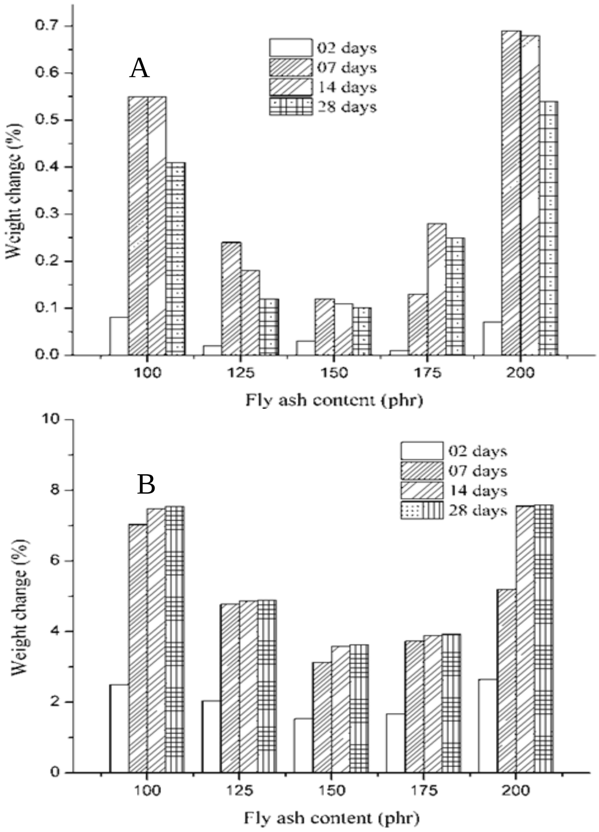

Figure 8: Changes in weight after acid chloride resistance test (A) and Changes in weight after sodium hydroxide resistance test (B)

REFERENCES

1. G. Martinez-Barrera, W. Brostow. *Effect of marble particle size and gamma irradiation on mechanical properties of polymer concrete*, E-Polymers, **61**, 1-14 (2010).
2. I. Duque-Ingunza, R. López-Fonseca, B. Rivas, J. I. Gutiérrez-Ortiz. *Synthesis of unsaturated polyester resin from glycolysed postconsumer PET wastes*, J. Mater. Cycles. Waste. Manag., **15**, 256-263 (2013).
3. B.W. Jo, S.K. Park, J.C. Park. *Mechanical properties of polymer concrete made with recycled PET and recycled concrete aggregates*. Constr. Build. Mater., **22**, 2281-2291 (2008).
4. Lokuge W. P., Aravinthan T. *Mechanical properties of polymer concrete with different types of resin*, Proceedings of the 22nd Australasian Conference on the mechanics of structures and materials, Sydney, Australia (2012).
5. F. Mahdi, H. Abbas, A. A. Khan. *Strength characteristics of polymer mortar and concrete using different compositions of resins derived from post-consumer PET bottles*, Constr. Build. Mater., **24**, 25-36 (2010).
6. M. E. Tawfik, S. B. Eskander. *Polymer concrete from marble wastes and recycled poly(ethylene terephthalate)*, J. Elastom. Plast., **38**, 65-79 (2006).
7. F. Awaja, D. Pavel. *Recycling of PET*, Eur. Polym. J., **41**, 1453-1477 (2005).
8. H.T. Vo, C. N. Hoang. *Glycolization of polyethylene terephtalate (PET) from waste bottle by diethylene glycol (DEG)*, Sci. Tech. Dev., **11**, 93-99 (2008).
9. J. R. Fried. *Polymer Science and Technology*, Proceedings of Prentice Hall PTR Conference Englewood Cliffs New Jersey (1995).
10. U. R. Vaidya, V.M. Nadkarni. *Unsaturated polyester resins from poly(ethylene terephthalate) waste. 1. Synthesis and characterization*, Ind. Eng. Chem. Res., **26**, 194-198 (1987).
11. P. Đ. T. Văn, H. P. A. Trương, T. V. Nguyễn. *Tái chế nhựa polyethylene terephthalate (PET) và ứng dụng nhựa đã qua tái chế*, Tạp chí Khoa học Trường Đai học Cần Thơ, Phần A: Khoa học Tự nhiên, Công nghệ và Môi trường, **39**, 57-65 (2015).
12. G. P. Speranza, R. A. Grigsby, M. E. Brennan. *Liquid phase polyols which are alkylene oxide adducts of terephtalic esters from recycled polyethylene terephalate*, In United State Patent Patent, 4485196 (1983).
13. M. H. Kamarudin, A. Z. Romli, M. H. Abidin. *The evaluation of eggshell particulate size in unsaturated polyester via mechanical test*, Proceedings of Malaysia Polymer International Conference: IOI Resort, Putrajaya (2009).
14. K. Saravana Raja Mohan, P. Jayabalan, A. Rajaraman. *Properties of fly ash based coconut fiber composite*, American J. Eng. Appl. Sci., **5**, 29-34 (2012).
15. N. Halacheva, P. Novakov. *Preparation of oligoester diols by alcoholytic destruction of poly(ethylene terephthalate)*, Polymer, **36**, 867-874 (1995).
16. C. H. Chen, C. Y. Chen, Y. W. Lo, C. F. Mao, W. T. Liao. *Studies of glycolysis of poly(ethylene terephthalate) recycled from postconsumer soft-drink bottles. II. Factorial experimental design*, J. Appl. Polym. Sci., **80**, 956-962 (2001).
17. C. H. Chen, C. Y. Chen, Y.W. Lo, C. F. Mao, W. T. Liao. *Studies of glycolysis of poly(ethylene terephthalate) recycled from postconsumer soft-drink*

bottles. I. Influences of glycolysis conditions, J. Appl. Polym. Sci., **80**, 943-948 (2001).

18. C. H. Chen. *Study of glycolysis of poly(ethylene terephthalate) recycled from postconsumer soft-drink bottles. III. Further investigation*, J. Appl. Polym. Sci., **87**, 2004-2010 (2002).
19. A. International. *ASTM D7029-09. Standard test method for determination of reactivity of unsaturated polyesters and vinyl esters at 180.0F [82.2°C]*, In ASTM volume 08.03 Plastics (III): D5117 - latest; Reinforced plastic piping systems and chemical equipment; Plastic Building Products **08.03** (2009).
20. Y. J. Huang, J. S. Leu. *Curing of unsaturated polyester resins. Effects of temperature and initiator: 1. Low temperature reactions*, Polymer, **34**, 295-304 (1993).

Corresponding author: **Bui Duy Du**
Institute of Applied Material Science
No 1A, TL29 Street, Thanh Loc ward, District 12, Ho Chi Minh City, Vietnam
E-mail: vina9802@gmail.com; Telephone: +84931797968.