Effects of Recycling Cycle on Used Thermoplastic Polymer and Thermoplastic Elastomer Polymer

Yu Lih Jiun[1*], Cher Tien Tze[1], Usaid Moosa[1], and Mou'ad A Tawawneh[2]

[1]Faculty of Engineering, Technology and Built Environment, UCSI University, Kula Lumpur Campus (North Wing), Lot 12734, Jalan Choo Lip Kung, Taman Tayton View, 56000 Cheras, Kuala Lumpur, Malaysia

[2]Department of Physics, College of Science, Al-Hussein Bin Talal University, Ma'an, P.O Box 20, Jordan

SUMMARY

Due to several environmental problems arising through the disposal of polymers, recycling has been growing rapidly as one of the best approaches to minimize environment pollution issue. Apart from the positive impacts towards environmental sustainability, recycling polymer is also benefiting in terms of manufacturing cost reduction, energy conservation and material resource conservation. The aim of this study was to investigate how recycling cycle affects the physical properties and mechanical properties for both used thermoplastic polymer and thermoplastic elastomer polymer. Samples were prepared by melting used polymers via melt blending technique. Results showed that tensile strength and density were decreased for thermoplastic polymer and the changes in visual are significant when the number of recycling cycle was increased. Tensile strength, yield strength and Young Modulus of thermoplastic elastomer are independent from number of recycling cycles. Presence of antioxidant fillers in thermoplastic elastomer enhanced the tensile strength (28.23%) and Young Modulus (29.16%) when the polymers were exposed to ultraviolet light.

Keywords: Recycling, Mechanical properties, Thermoplastic polymer, Thermoplastic elastomer polymer

1. INTRODUCTION

At present, incineration and landfill are the common municipal waste plastic management methods. The first method by incineration has negative impact towards environment in terms of hazardous gases and compounds release such as nitrous oxide, sulphur oxides, dust, dioxin and other toxin[1]. While the latter one, landfill method is facing limited landfill disposal capacity issue as the plastic wastes have higher resistivity towards degradation and the volume of disposal waste plastics are in incremental momentum per annum. Recycling of plastic wastes has become an alternative method in waste management which lessens the direct negative impacts on environmental pollution problem caused by incineration and landfill. Furthermore, recycling of plastic wastes can contribute in energy conservation and material conservation from the processes of refining fossil fuels into virgin plastic[2,3]. However, it has been a challenge in establishing a cost effective recycling plastic waste system due to the complexities inherent in the reuse of polymer in terms of segregation of types of polymer and treatment processes that are required. Therefore, most of the plastic waste is being recycled via primary recycling techniques, which involved utilization of scrap plastics that have similar features to the origin products[3].

In thermoplastic polymer manufacturing industry, the thermoplastic polymer plastic edges and parts are being recycled via extrusion and are pelletized before reintroducing into the production process. In Europe at year 1997 to 2002, there was an increase of 10% in plastic waste generation in packaging[4]. The unique properties of high density polyethylene (HDPE) in terms of rigidity, superior mechanical strength, higher service temperature limits[5] and excellent process ability offers wide application to the consumers. The common application of HDPE includes: tare and package, consumer and household commodities, pipes, insulation cable and other related product[6]. Due to its feasible usage and process ability, HDPE utility volume is increased annually and became one of third largest commodity plastic material in the world, ranked after polyvinyl chloride and polypropylene[7].

Corresponding author: y_jiun@hotmail.com

There are numerous studies done on the recycling effects on polyethylene in terms of its mechanical properties which includes virgin HDPE[4,8], mixture of HDPE with additives[9-12] and composite[13].

Besides thermoplastic polymer, there are many potential polymers that can be recycled. A rising of the utilization of thermoplastic elastomer in the application of automotive, building and constructions, wires and cables are giving significant impact towards the environment. Thermoplastic elastomer's properties and functional performance similar to those of a conventional vulcanized rubber; yet it still can be processed in a molten state as a thermoplastic polymer. Because of their unique mechanical properties, they are now gradually replacing conventional vulcanized rubber or elastomer in the market[14]. Automotive parts like bumpers, body panels, dashboards and door claddings are nowadays made out of advanced polypropylene (PP) materials. Most of the time, heterophasic blends are used where PP is the continuous phase and an ethylene-propylene copolymer (EPR) the dispersed one. The polypropylene matrix delivers the stiffness of the material whereas the rubbery inclusions act as impact modifiers providing a grade with balanced stiffness-impact behavior[15]. There are limited studies done on the recycling effect of blends of thermoplastic elastomer. The changes in properties of recycled thermoplastic elastomer need to be considered as one of the most important factors in recycling. Since specific properties are required for each application, the changes in properties that occur during the recycling process might lead to the material being unusable or not safe to be used.

In view of limited studies had done on the recycling effects on thermoplastic elastomers,. In this paper, we prepared the thermoplastic elastomer samples with melt blending technique. The impact recycling cycle and ultraviolet exposure on mechanical properties was investigated. Thermoplastic polymers samples were prepared under same condition, and their properties were compared with thermoplastic elastomers.

2. MATERIALS AND METHOD

A thermoplastic polymer (TP): used high density polyethylene (HDPE) packaging and a thermoplastic elastomer polymer (TPE): used ethylene-propylene copolymer (EPR) car bumper as were collected and cut into small pieces of 5 mm × 5 mm × 1 mm. Both polymers were melted by using melt blending technique in Cole-Parmer StableTemp block heater at temperature of 180 °C for 15 min. Sample preparation was done by using a compression molding with 1 MPa load for 15 min. The amount of needed resin was weighed and was compressed into strip of 1mm thickness according to ASTM D882-09 specimen and test standards. The specimens were then tested for physical and mechanical properties. Tensile machine Tinius Olsen H50KT was used. Density test was done by using Archimedes principle. For second cycle sample preparation, used samples were crushed into granular form then went through the melting and compression molding process. Similar sample preparation and testing processes were repeated up to five cycles. For ultraviolet degradation study, first cycle samples were exposure at outdoor environment for one week, and then their physical and mechanical properties were tested.

3. RESULTS AND DISCUSSION

Figure 1 shows the effect of recycling number on density of both thermoplastic polymer and thermoplastic elastomer. It can be seen that the density of thermoplastic polymer is in a decreasing trend as the recycling number is increased. This result is consistent with earlier reports[8,16-17]. About 2.1% density was reduced from the first recycling number to the fifth recycling number. The process of recycling involved crushing and melting lead to chain scissoring in the polymer chains. Furthermore, thermal degradation involved in the melting process contributed to the weakening of intermolecular forces between the polymer chains[18]. Some polymer chains with smaller molecules, resulted from the chain scissoring, were generated into volatiles products[18] and released into the atmosphere during melting process. It was found that reduction of crystallinity as one of the side effect of repeating recycling polymer, linked to the chain scissoring effects[8].

As for thermoplastic elastomer, the density does not follow the same trend as thermoplastic polymer. The fluctuation in the densities as the recycling number increases might due to the changes of cross-linking density formed in the polymers. It has been known that the thermoplastic elastomers are co-polymers of two or more different monomers consist of multiple branches connected to the main chain[19]. The crushing and melting process during recycling is distorting the regular formation of copolymer chains where the polymer branches joining back to the main chain at different position[19] with different length, resulting alteration in the mass per volume upon solidification.

Effect of recycling number on tensile strength and yield strength for thermoplastic polymer and thermoplastic elastomer were shown in **Figure 2**. Relating yield strength with recycling cycle, higher yield strength is required as the recycling cycle increased. In view of yield strength against recycling cycle, the yield strength increases 3.3 times from first recycling cycle (2.16 MPa) to fifth recycling cycle (7.22 MPa) for thermoplastic polymer. These results are in contrast with earlier

Figure 1. Effect of recycling number on density of polymer

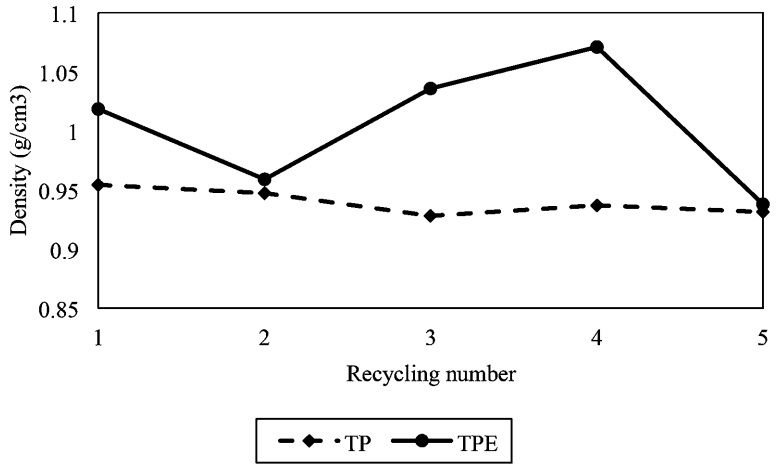


Figure 2. Effect of recycling number on tensile strength and yield strength

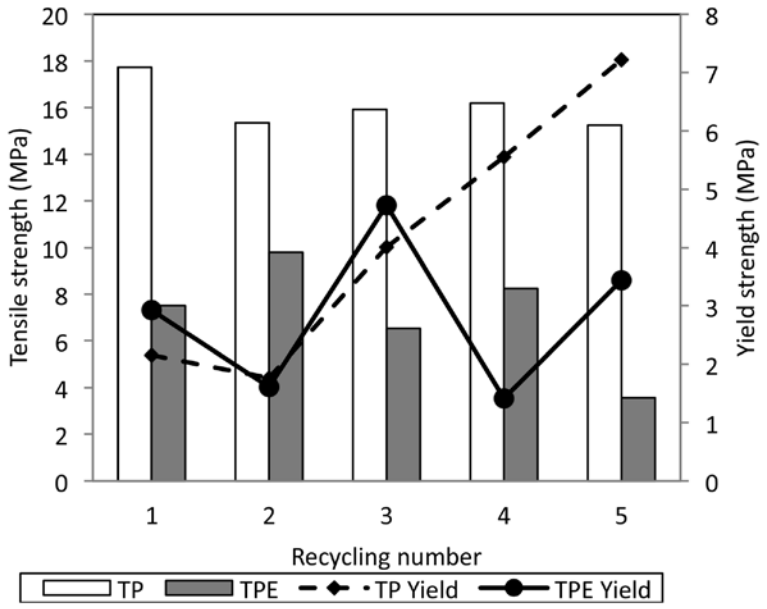
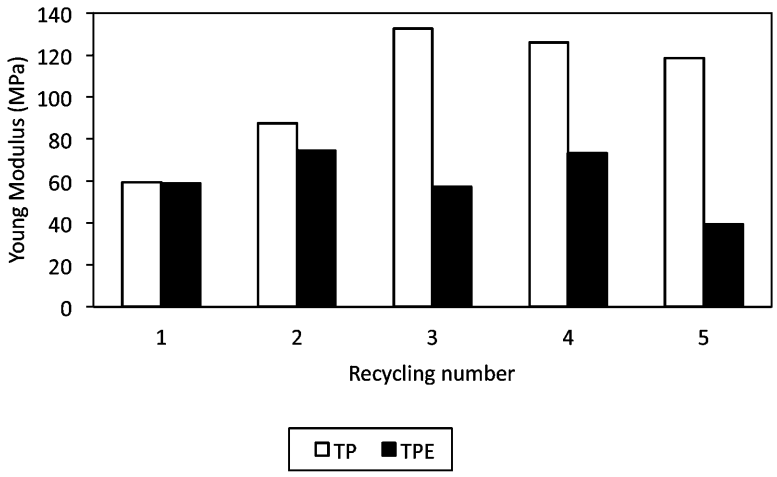


Figure 3. Effect of recycling cycle on Young Modulus



reported study[8] where it showed low difference of 4% yield stress increased with the recycling cycle in high density polyethylene. Yield strength is defined as stress at which it begins to deform[20]. In order for the polymer to deform, it require constant addition of tensile strength to keep pulling it until it reaches a phase where it is over pulled or stretch that it could not be return back into its original shape. Thermal degradation induced from recycling process interrupt the effective stress transfer through chain scissor fragmental polymer. Therefore led to higher yield strength. HDPE with C_3-C_5 carbons has higher yield strength after undergoing catalytic degradation[21]. This is relying on the polymer's elongation capabilities to return back to its own shape.

For thermoplastic elastomer, neither tensile strength nor yield strength is affected by the increment of recycling cycle, obtaining a mean value of 2.82 MPa for yield strength and 7.13 MPa for tensile strength.

Young Modulus of thermoplastic and thermoplastic elastomer polymers were shown in **Figure 3**. The Young Modulus of thermoplastic polymer from its first cycle is 59.22 MPa, has increased to a peak value at 132.52 MPa in third cycle, then reducing gradually in the following cycles. Initial recycling of thermoplastic polymer from first cycle to third cycle with reducing molecular weight, induced an increase in the crystallinity level and as a consequence in the increase of the Young Modulus[22]. Further increment of recycling cycles has direct impact on the elongation of thermoplastic polymer. The chain scissoring as the consequences from thermal degradation is weakening the molecular bonding in between the polymers. Hence, the polymers are prone to elongate when the recycling cycles repeated for several times. Young Modulus is defined as the ratio of stress over strain. When the increment of strain suppressed stress, the Young Modulus will decrease.

From our findings, the elongation of thermoplastic polymer molecules becomes more dominant after third recycling cycle. Therefore, a marginal 4.95% and 5.94% reduction in Young Modulus were observed after third recycling cycles.

In contrast, the values of Young Modulus obtained from thermoplastic elastomer are independent from the recycling cycle. Ethylene-propylene copolymer consists of polyolefin semi-crystalline thermoplastic and amorphous elastomeric component. The co-continuous phase system with the hard phases providing the strength and the soft phase providing the flexibility[22]. The scissoring effect induced from thermal degradation attributed to random arrangement of crosslinked thermoplastic elastomer molecules with weak intermolecular bonding. Hence, thermoplastic elastomer which consists of different length of molecular chains is forming soft phase and hard phase, giving a mean Young Modulus value of 60.62 MPa. The results are consistent with earlier reports[23] where their results indicated that the Young Modulus of acrylonitrile-butadiene-styrene copolymers is independent from recycling degradation.

Table 1 showed the comparison of mechanical properties of first cycle polymers before and after ultraviolet light exposure. In comparison, the ultraviolet degradation of both thermoplastic polymer and thermoplastic elastomer, the density of both polymers had decreased. It was observed that ultraviolet degradation had given similar impact towards thermal degradation of the recycled thermoplastic polymers where tensile strength was decreased and yield strength was increased. An insignificant 2.27% of reduction in Young Modulus value indicating that thermoplastic polymer chains are bonded by weak intermolecular bonding. The visual color of thermoplastic polymer were observed that it had changed from clear white color to cloud color (**Figure 4(a)**) from first recycling cycle to fifth recycling cycle, due to thermal-oxidation effect.

Peroxides, carbonyls, chain branches and unsaturated structures are the four possible weak link structures induced from thermal oxidation[24]. For an automotive application, antioxidant filler are suggested which works by absorbing the UV radiation preventing it from reaching the bulk of the polymer and converting this to energy thus preventing the discoloration and delamination of the surface of the polymer[25]. The addition of antioxidant fillers, acting as an oxygen-centred radical scavenger, inhibits auto-oxidation as soon as it starts, thus enhancing the thermo-oxidative stability. Therefore, tensile strength and Young modulus of thermoplastic elastomer had shown improvement after ultraviolet exposure, attributed to the presence of antioxidant fillers in its compound. A reduction of 10.58% yield strength after exposure of ultraviolet was showed by thermoplastic elastomer. The discoloration occurred in thermoplastic elastomer (shown in **Figure 4(b)**) corresponding to the recycling cycle and ultraviolet exposure are attributed to color pigment degradation in the polymer.

Figure 4. (a) Color changes of TP and (b) TPE as recycling number increases

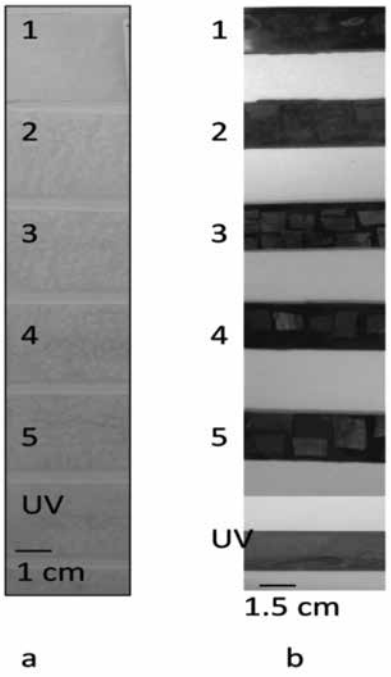


Table 1. Comparison of mechanical properties polymer before and after exposure of ultraviolet light

Sample	Density (g/cm^3)	Tensile strength (MPa)	Changes (%)	Yield strength (MPa)	Changes (%)	Young Modulus (MPa)	Changes (%)
TP (Before)	0.95	17.60	-29.32	3.79	+43.80	77.46	-2.27
TP (After)	0.92	12.44		5.45		75.70	
TPE (Before)	1.02	7.51	+28.23	2.93	-10.58	58.72	+29.16
TPE (After)	1.00	9.63		2.62		75.84	

4. CONCLUSIONS

Thermal degradation has different impact towards thermoplastic polymer and thermoplastic elastomer. For thermoplastic polymer (HDPE), when the recycling cycle was increased, density, tensile properties and Young Modulus were decreased, except yield strength. Ultraviolet degradation had the similar effect as thermal degradation. The yield strength of thermoplastic polymer had significant increased 43.80% after exposed to ultraviolet. For thermoplastic elastomers (EPR), their mechanical properties (tensile properties, yield strength and Young Modulus) were behaved differently as compared to thermoplastic polymers. Tensile strength, yield strength and Young Modulus of thermoplastic elastomer are independent from recycling cycles. However, presence of antioxidant fillers in thermoplastic elastomer enhanced the tensile strength (improved by 28.23%) and Young Modulus (improved by 29.16%) when the polymers were exposed to ultraviolet light.

REFERENCES

1. Sachin Kumar, A.K Panda, Singh R.K., *Resource, Conservation and Recycling,* **55**, (2011), 893.
2. Wang, CQ., Wang H., Liu YN,. *Waste Management,* **35**, (2015), 42.
3. Al-Salem, S.M. Lettieri, P., Baeyens., Waste *Management,* **29**, (2009), 2625.
4. Sanchez-Soto, M., Rossa, A., Sanchez, A.J. and Gamez-Perez J., *Waste Management*, **28**, (2007), 2565.
5. Abdel-Bary, E.M., Handbook of plastic films, Shropshire, UK, (2003).
6. Saisinchai, S., *.Eng. J.* **18**, (2013), 45.
7. Kreiger, M.A., Mulder, M.L., Glover, A.G., Pearce, J.M., *Journal of Cleaner Production*, **70**, (2014), 90.
8. Abo El-Khair, M.S., Ali, A.A., *International Journal of Modern Engineering Research (IJMER)*, **3**(2), (2013), 798.
9. Ahmed, N. and Khan, J.H., *The 6th Saudi Engineering Conference*, **2**, 359, Dhahran, (2002), KFUPM.
10. Mastral, J.F., Berrueco, C., Gea, M., Ceamanos, M., *Polymer Degradation and Stability*, **91**, (2006),3330.
11. Achilias, D.S., Roupakias, C., Megalokonomos, P., Lappas, A.A., Antonakou, E.V., *Journal of Hazardous Materials*, **149**, (2007), 536.
12. Deka, B.K., Maji, T.K., *Composites: Part A*, **42**, (2011), 686.
13. Attwood, J., Philip, M., Hulme, A., Williams, G., Shipton, P., *Polymer Degradation and Stability*, **91**, (2006), 3407.
14. Chatterjee, K & Naskar, K., *eXpress Polymer Letters* **1**(8), (2007), 527.
15. Grestenberger, G., Potter, G.D., Grein, C., *eXpress Polymer Letters* **8**(4), (2014), 282.
16. Bozorg-Haddad, A., Iskander, M., Chen, Y.F., *Construction and Building Materials*, **26**, (2012), 505.
17. Boldizar, A., Jansson, A., Gevert, T., Moller, K., *Polymer Degradation and Stability*, **68**, (2000), 317.
18. Singh, B and Sharma, N., *Polymer Degradation and Stability* **93**, (2008), 561.
19. Shanks, Robert A & Kong, Ing.. Advances in Elastomers: Blends and Interpenetrating networks, **11**, (2013), 11.
20. Roylance, D., Mechanical properties of materials., New York, US, 2008.
21. Panda, A.K., Singh, R.K., Mishra, D.K., *Renewable and Sustainable Energy Review*, **14**, (2010), 233.
22. Kostadinova Loultcheva, M., Proietto, M., Jilov, N., La Mantia, F.P., *Polymer Degradation and Stability,* **57**, (1997), 77.
23. Arostegui, A., Sarrionandia, M., Aurrekoetxea, J. & Urrutibeascoa, I. *Polymer Degradation and Stability,* **91**(11), (2006), 2768.
24. Peterson, J.D., Vyazovkin, S., Wight, C.A., *Macromolecular Chemistry and Physics*, **202**, (2001), 775.
25. Decker, C., Biry., *Progress in Organic Coatings*, **29**(1-4), (1996), 81.