FTIR CHARACTERISATION AND STRENGTH PERFORMANCE OF DEGRADABLE ADDITIVE INCORPORATED POLYETHYLENE TEREPHTHELATE (PET) BOTTLE UPON EXPOSURE TO DIFFERENT ENVIRONMENT

[1]RAHMAH MOHAMED, [2]MOHD MUIZZ FAHIMI, [3]FATIN AFIQAH JUHARI, [4]AHMAD MAWARDI RAHMAT, [5]SITI AISHAH MOHD ISA

[1,2]Faculty of Applied Sciences (FSG), UniversitiTeknologi Mara,
UiTM Shah Alam, Malaysia
E-mail: [1]rahmahgepsb@gmail.com, [2]fatinafiqahjuhari@gmail.com, [3]muiesfahimiey@yahoo.com,
[4]adirahmat1617@yahoo.com, [5] marsha8990@gmail.com

Abstract— Effect of degradable incorporated masterbatch Polyethylene Terephthelate (PET) on strength and structural changes of PET upon exposure for highly demanded bottle packaging are investigated here. Bottle for beverages packaging normally use Polyethylene Terephthalate (PET) due to excellent characteristic such as neligible permeability to carbon dioxide, can withstand high temperature, non-toxic nature, high mechanical strength and transparency. Masterbatch of Polyethylene Terephthalate (PET) were injection moulded as preform and blow moulded in bottle manufacturing. Mechanical properties example tensile strength, elongation and modulus were tested before and after exposure towards three different conditions which are at room temperature, exposed to sunlight and in ridge; using two different filling liquid namely mineral water and coke. Bottles were exposure or four week period and result was taken. It was found that for PET filled mineral water the reduction of PET tensile strength was about 50% in strength of sample after exposed to sunlight after 4 weeks while in fridge, tensile was around 7.27 as compared to room temperature exposed PET is 11.96. Strength before exposure which is about 13.01 do not show much difference as compared to RT sample. Hence, condition of exposure did affect the strength performance. Sample of exposed PET towards sunlight has greater reduction in strength; presence of UV light from sunlight and cooling PET at low temperature was found to reduce strength. Temperature had an effect and exposure to low temperature is subjected to de-annealing process. Structural characteristic via Fourier Transform Infrared Spectroscopy (FTIR) was performs to investigate structural features of the molecular bond of degradable PET bottle. Greater intensity of aldehyde and ketone absorption were found for exposed bottle to sunlight compared to other conditioned bottle. For sunlight exposure, wavenumber were shifted to lower wavenumber from 1753 and 1614 to 1707 and 1577 cm-1.

Keywords— Polyethylene Terephthalate (PET), Mechanical Strength, Fourier Transform Infrared (FTIR) Analysis.

I. INTRODUCTION

Up to now, Polyethylene Terephthalate (PET) are still popular as packaging for beverage and food due to excellent characteristics such as negligible permeability to carbon dioxide, can withstand high temperature, non-toxic nature, lack of influence on flavour, high mechanical strength and high transparency [1] . PET materials do not degrade and are mostly recycled, so that it will not be decomposed. However the development of natural additives as degradant by Rahmah et al, had introducted the addtives for PET [2]. The addition of natural additives was incorporated into PPresin formulation for enhancing this degradability [3].
Strength and thickness of bottle is utmost importance as it act as holding strength for liquid or beverage. Testing of related strength and performance of PET bottles need to be investigated and taste for filled beverage need to be evaluated to maintain its quality. Nowadays, the virgin of PET bottles has high tensile test, drop test and good texture and can withstand different temperature without compromise its function. Therefore, this testing will assist to investigate that the effect of the incorporation of new PET masterbatch to bottle strength and structural changes. Bottle strength of filled water or drink contained in the bottle is investigated upon exposure to different conditions for certain period of time.

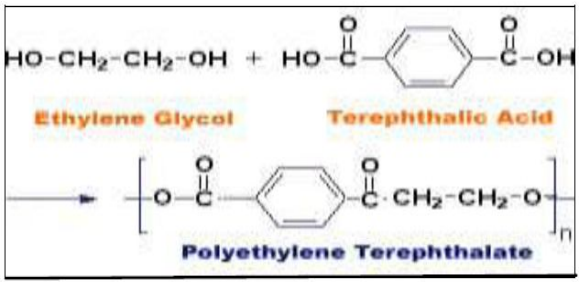


Fig.1. Reaction process for manufacturing Polyethylene Terephthalate

Bottles for mineral bottles and carbonated drinks are largely from PE, PP, or PET. However, PET is most popular as it can withstand high temperature, non-toxic nature, lack of influence on flavour, high mechanical strength, high transparency and low Oxygen and Carbon Dioxide diffusion. According to Bach et al., 2014 temperature and the presence of CO2 increased the release of formaldehyde, acetaldehyde and antimony (Sb) but just in small amount [4]. PET can withstand carbonated drinks as well as mineral waters. Juices are normally filled with PE or PP bottle. To select the material that better

matches quality objectives, shelf life, storage temperature and costs of the product PET packaging materials are preferred for bottling. Because of its excellent mechanical properties, its clearness, UV resistance and good oxygen barrier properties, PET (polyethylene terephthalate) is increasingly used in bottles manufacturing for juices [5]. After the bottles blown, a sample bottles testing will filling with different type of beverages. According to 6, When the bottle was exposed to sunlight, it does not destroy disease-causing microorganism found in the water but also transform the plastic material into photoproducts [6].

PET has higher tensile strength than many other general purpose packaging plastics like polyolefins, PVC, etc. For example, HDPE has a tensile strength between 31- 45 MPa while PET can have it between 48.2- 72.3 MPa [7] Deformation under stress at elevated temperature.

Strength and performance are interrelated. Studies of strength performance using four different materials with PET bottle as comparison had been performed. Thermal, mechanical and barrier performance of SiOx coated PLA bottles produced with the PlasmaxTM process against poly(ethylene terephthlate) (PET) bottles were investigated. Parval found mechanical performance of the bottles on the basis of tensile and compression strength showed relativly small chages in tensile with changes in period of exposure for PET compared to PLA or PLA coated SiOx. It affects not only its mechanical strength, but also transmission OVTR and Tg upon filling with different beverages [8].

Aging is essentially synonymous with oxidation [9].There are important differences between this type of aging and physical aging. It is well known fact that, oxidation degrades all mechanical properties. Impact resistance may be the first property to show evidence of decline, but others will follow eventually. Physical aging reduces ductility but will improve load-bearing properties such as strength, modulus, and creep resistance. Oxidation will eventually result in a reduction in molecular weight; it is a chemical process that breaks the polymer chain. Physical aging causes no such disruption of the polymer building block.

Works on natural weathering tests had been carried out by exposing plastics such as PE film. After some periods of exposure samples are taken and then tensile properties are measured. Loss of these properties is taken as a measurement of degradation [10]. Degradation of polymers due to weathering manifests as physical and chemical changes. Plastic materials show some degree of degradation upon exposed to weathering factors. Test results of the exposed material must be taken as indicative only and exposure results can provide an indication of relative outdoor performance. Factors to take account are geographic location, temperature, wind and moisture are factors very important in the UV degradation process of polymer

II. DETAILS EXPERIMENTAL

2.1 Materials and Procedures

The materials and methodology examined in this project are stated below

a) Polyethylene Terephthalate (PET) preform

The PET preform was prepared via injection moulding and then will be blow moulded. Then, this preform will be blown to form 1.5 litre bottle shapes.

b) Mineral Water

All the mineral water will be filled up to 1 litre bottle of mineral water 3 set condition. One condition are for bottles filled with 1 litre mineral water. One bottle is for BOD sample and another bottle is for exposed filled PET bottles testing. Determinations of PET bottle filled water content were performed for mineral water bottle stored at different temperatures and exposed to sunlight.

c) Carbonated Water

The carbonated water also were also prepared for three 3 different condition using namely COKE for carbonated drink. The effects of alkali water towards the PET bottle filled beverage after storage at different temperature and exposed to sunlight were performed.

d) Testing of filled beverages in PET bottles

All the bottles were exposed to 3 sets of condition, under Sunlight, room temperature and fridge ~ 10°C for maximum of 4 weeks. FTIR for PET bottle were analysed using FTIR Perkin Elmer *Spectrum* One under scan transmission mode ranging from 600 to 4000cm^{-1}. Spectrum were analysed for both exposed and unexposed PET bottle

III. RESULTS AND DISCUSSION

These bottles had been exposed to sunlight and at different temperature such as room temperature and cooling in fridge for one month. The weather condition for sunlight are for July month under Malaysian weather with humidity above 70%. Cool temperature attained by storing in fridge were about 10°C. Room temperature in Malaysia is about 27°C.

3.1. Tensile Test

The tensile tests have been performed on the compressed film (2 mm thickness) of sample after exposed to sunlight, room temperature and fridge. The sample was taken from bottles that have been exposed at different condition for maximum 4 weeks. During the tensile test, the load elongation curve was obtained by using a Tensile Tester Testometricwith a 20kN load cell and a crosshead speed of 10mm/min. All tests were performed at room temperature

according to ASTM D 638. The tensile strength, Young's Modulus and Elongation at break of modified Polyethylene Terephthalate at different conditions were discussed in this section. The data of Tensile properties are shown in the table 1 below.

Table 1. Tensile properties of PET bottle before and after exposure

	Before Exposed	Room Temp	Fridge	Sunlight
Tensile strength (MPa)	13.01	11.96	7.27	6.14
Elongation at break (mm)	0.48	0.33	0.25	0.22
Young Modulus (N/mm^2)	4035	3679	6810	4684

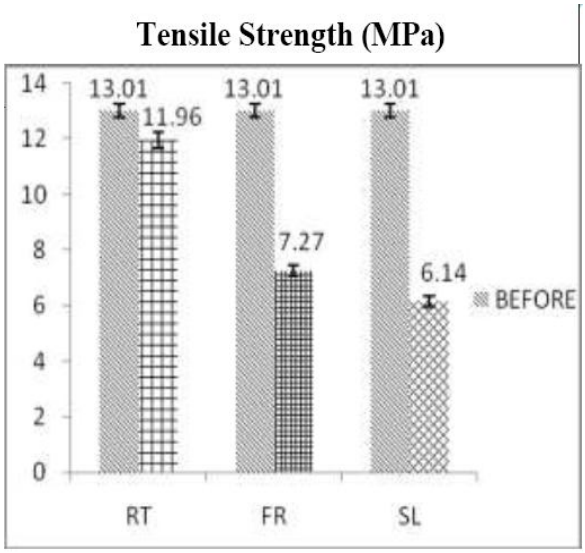


Fig. 2. Tensile strength of modified PET bottles after exposed at different condition

Figure 2 shows the result of tensile testing of modified PET bottles from different exposure condition. The strength before exposure was resulted of 13.011 MPa. Tensile strength of modified PET bottles at room temperature show the highest result which is 11.962 MPa compared to exposure to sunlight and Fridge. Initially, at room temperature, the PET chain are well organized and aligned which depicted in their higher tensile strength as opposed to bottle PET which are exposed to UV exposure and lowered temperature as in sunlight and fridgerespectively. After exposing to sunlight, the tensile strength of bottles is 6.14 MPa which showed the lowest result. Tensile strength reduction observed to be approximately 50% from the original.

The molecular structures exposed with UV – light resulted in its structure changed. UV - light had attacked its chain and causes chain scission thus lowering the strength of bottles. Tensile strength of bottles after stored at fridge also shows reducing in strength which is 7.27 MPa. The lower temperature exposure seems to reduce bonding interaction of PET and remaining additives. Therefore, it could be said that, lower temperature condition had resulted in lower tensile strength of modified PET bottles. Temperature had an effect and exposures to low temperature as they are subjected to de - annealing process. Annealing processing may involve chain alignment as it is exposed to high temperature while Freezing could affect chain disorientation and disordered arrangement of PET chain [11].

3.2. Elongation At Break

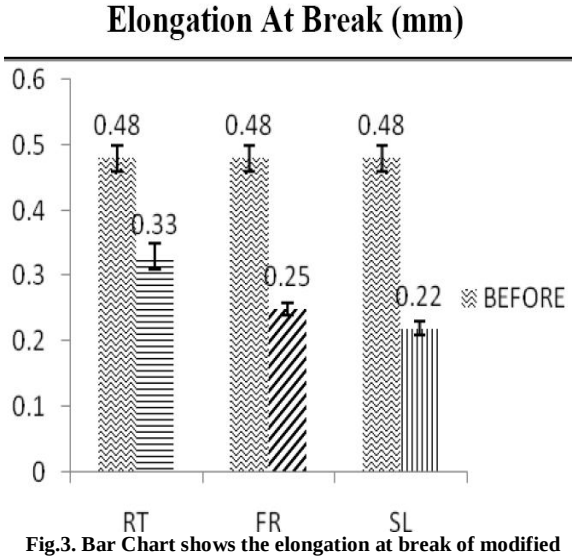


Fig.3. Bar Chart shows the elongation at break of modified PET bottles after exposed at different condition

For elongation at break, the elongation –to – break is the strain on a sample when it breaks. Elongation at break refers to how amount of stress needed to break the polymer.

Based on the data above, the elongation at break before exposure was of 0.48 mm. The highest elongation at break was obtained by a sample that exposed at room temperature which is 0.33 mm compared than sample was exposed at sunlight and fridge which are 0.22 and 0.25 respectively. At room temperature, not much changes in Elongation at break which is about 20% reduction. Sample in fridge show higher reduction which 60% due to low temperature that can lead to slow crystallization thus make a sample less tough. High amount of temperature and too low temperature are caused the polymer chain changed from normal ordered structure. Therefore, it will tend to reduce the elongation at break of the sample. After that, the UV from sunlight was break down the molecular structure of modified PET bottles causes chain scissoring [12]. Thus, this deterioration of long chain in polymer chain causes sample at sunlight were resulted low toughness. The sample at room temperature did not have any molecular break down thus it has ability to stretch and elongate so that increasing the elongation at break of the sample.

3.3. Young's Modulus

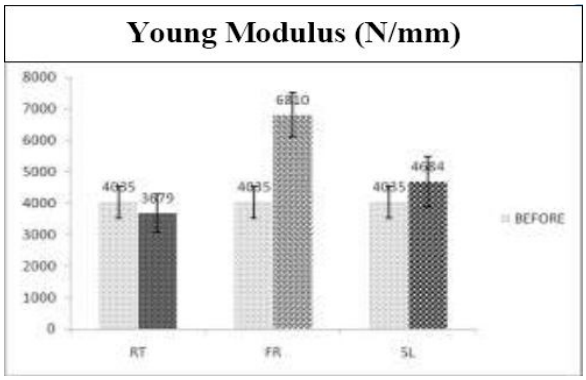


Fig.4. Bar chart showing the Young's Modulus of modified PET bottles after exposed at different condition

Based on the data of Young's Modulus (N/mm^2) above, for 4 weeks of environmental exposure, sample in the fridge has the most brittle than sample at the sunlight and room temperature which is 6810 N/mm^2 and sample at room temperature has the lowest which is 3679 N/mm^2.

Young's Modulus before exposure shown at 4035 N/mm. In fridge, the sample shows increasingly approximate 60% in their Young's Modulus. It can be said that, the sample at the fridge was the highest brittle compared than other sample. In sunlight, only 10 % increase in their Young Modulus due to the molecular polymer in the sample at sunlight still has a crystal. The low temperature in the sample at fridge was stuck the growth of crystal in the bottles film causes high brittle.

Based on tensile properties above, the different in these properties with different condition was due to presence of additive and UV sunlight act to assist degradation The UV from sunlight attack the molecular chain with the presence of additive may causes molecular chain scission of the polymer. Long chains of polymer break down into short chain which allowed degradation to occur. This can be seen in the table 1 above whereas the samples at sunlight have low strength compared than sample in fridge and at room temperature. PET in Fridge has lower elongation at break than another sample at room temperature and sunlight due to frozen in orientation and brittleness of the PET chain at low temperature.

3.4. Fourier Transform Infrared (FTIR) Analysis

Fourier Transform Infrared (FTIR) Spectroscopy was used to analyze and investigate the relation of molecular structure in the modified PET bottles film after exposed at different conditions. The sample was used is the thin film with dimension (2 x 2) cm. The FTIR spectra of the molecules in sample at sunlight, room temperature and fridge were varied slightly as a result of different composition and interaction between different conditions. The range for the wave number used in FTIR determination of these samples is from 600 cm^{-1} – 4000 cm^{-1}. The spectra were recorded in the transmittance.

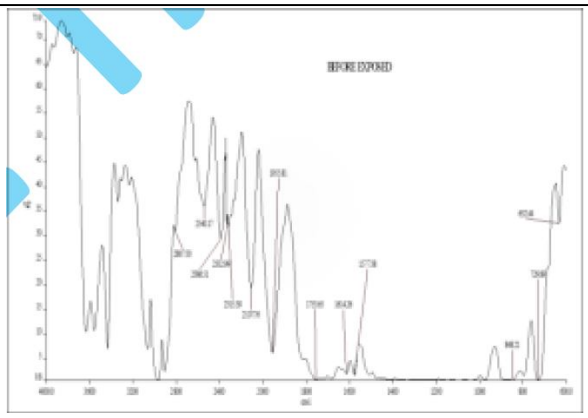


Fig.5. The sample of modified PET bottles before exposed

Fig.6 below shows the interaction of bond in the degradable PET bottles after exposed for four weeks at different condition. The peaks were shown are most likely the same. The highest peak shown between 1750 cm^{-1} – 1700 cm^{-1} is the primary C=O bonds. This came from the main structure of aldehyde in Polyethylene Terephthalate (PET) itself as mentioned in the literature review. This highest peak was TThe fig.6 above shows the interaction of bond in the degradable PET bottles after exposed four weeks at different condition. The peaks were shown are most likely the same. The highest peak shown FTIR Characterisation and Strength Performance of Degradable Additive Incorporated Polyethylene Terephthelate (PET) Bottle Upon Exposure to Different Environment.

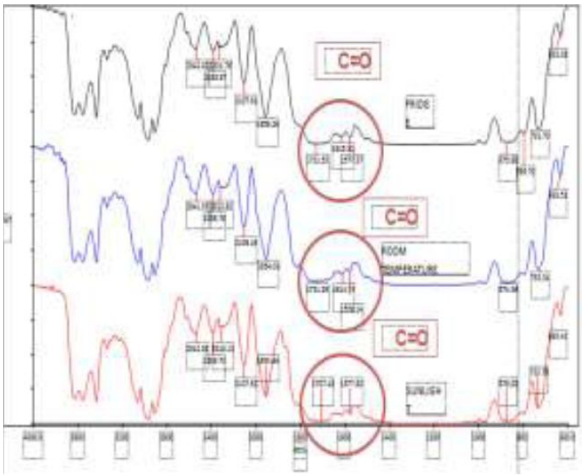


Fig.6. The sample o modified PET bottles after storage at Room Temperature, Sunlight and fridge

Table 2 Related wavelength and bonding that present in FTIR

Wavelength Range (cm^{-1})	Types of Bond
3400 – 2800	C – H stretching
1800 – 1500	C – O stretching
800 – 600	C – H bending

Between 1750 cm^{-1} – 1700 cm^{-1} is the primary C=O bonds. This came from the main structure of aldehyde in Polyethylene Terephthalate (PET) itself as

mentioned in the literature review. This highest peak was presence at the bottles that had been exposed at Fridge. Before exposed the bottles, the spectra was located at the 1753.65 cm^{-1} as shown in figure 6. However, after the bottles were exposed for 4 weeks,the spectra were shifted to ower wavelength, to 1731.29 for room temperature, 1731.53 cm^{-1} for fridge and 1707.43 cm^{-1} for Sunlight. These three peaks has different wavelength because the vibrational energy of the bonding changes of carbonyl group which are influenced by temperature and ultraviolet exposure. The wavelength at sunlight showed the lowest shift due to greater electrophilic pull by oxygen atom of carbon group upon free radical attack from UV light. Therefore, it can be said that the frequency of vibration of the molecules is directly proportional to the bonding .Spectra of aldehyde in sample at sunlight has high reduction because the UV light was had attacked the double bond of aldehyde. This is caused by lower interaction with main bond is effect of exposure of high temperature and UV light towards PET sample tends to reduce the amount of wavelength absorption in the sample.

CONCLUSIONS

From the present study, it can be concluded that degradation affects the tensile properties of PET bottles due to the result obtained from the tensile tests after exposure to sunlight and at two different temperatures. Changes in tensile properties were observed, some reduction of about 50% or more, based on exposure condition of the bottles. The results pointed out that the sample had been exposed to sunlight showed lower Tensile Strength,
Elongation at Break and Young's Modulus than sample exposed at room temperature and fridge. This is because the sample at sunlight with degradable additive had enhanced the degradation of the bottles upon exposure to UV light from sunlight. presence of UV light from sunlight and cooling PET at low temperature was found to reduce strength. Temperature had an effect and exposure to low temperature is subjected to de-annealing process. Structural characteristic via Fourier Transform Infrared Spectroscopy (FTIR) was performs to investigate structural features of the molecular bond of degradable PET bottle Improvement on the period of exposed should be longer to 6 – 8 weeks in order to investigate the amount of aldehydes/ketones presence in the beverage.

ACKNOWLEDGMENTS

The author gratefully acknowledges Faculty of Applied Sciences (FSG) and also UniversitiTeknologi Mara (UiTM) for the facilities and equipment in making this studies a success.

REFERENCES

[1] Frounchi, M., Mehrabzadeh, M., &Ghiaee, RStudies of Recycling of Polyethylene Terephthalate Beverages Bottles. 1997.
[2] Hopewell, J., Dvorak, R., &Kosior, E. Plastics recycling: challenges and opportunities. Philosophical Transactions of the Royal Society of London B: Biological Sciences, 364(1526), 2115-2126, 2009.
[3] Mohamed, R, Mohd, A.F., Abdullah, A.F..I., "Effect of Aging on Film Strength and Morphology of Natural Additive Polypropylene Packaging Film. J Mat SciEng, vol. 5, pp. 555-560, 2010.
[4] Ros-Chumillas, M., Belissario, Y., Iguaz, A., &López, A. Quality and shelf life of orange juice aseptically packaged in PET bottles. Journal of Food Engineering, 79(1), 234-242 ,2007.
[5] Wegelin, M., Canonica, S., Ibrahim, P., &Larroque, M. "Does sunlight change the material and content of polyethylene terephthalate (PET) bottles". Journal of water supply 2001.
[6] Wegelin, M., Canonica, S., Alder, C., Marazuela, D., Suter, M. F., Bucheli, T. D., ... & Ibrahim, P.. Does sunlight change the material and content of polyethylene terephthalate (PET) bottles?. Journal of Water Supply: Research and Technology-AQUA, 50(3), 125-135,2001.
[7] Selke, S., J.D. Culter, and R. Hernandez, "Plastics Packaging: Properties, Processing, Applications, And Regulations".Hanser Gardner Publications. 2nd ed. 2004.
[8] M.S Thesis, School of Packaging, Michigan State University 1998 – 2011. "Comparative Performance of PLA and PET Bottles for Alcohol and Sugar Acid Solutions". Praveen Rawal, 2011.
[9] Michael P. SepeLLC. "MATERIALS: The Mystery of Physics Aging: Part 1 from Plastics Technology Nov 2014.
[10] Considerations About WeatheringExposure And Uv DegradationOf Polymeric GeomembranesP.C. Lodi,BDS Bueno, J.G. ZornbergMinerva, 4(2): 201-205
[11] Kim, J. Y., Seo, E. S., Kim, S. H., &Kikutani, T. "Effects of annealing on structure and properties of TLCP/PEN/PET ternary blend fibers".Macromolecular Research, 11(1), 62-68. 2003.
[12] Rwei, S. P., Lin, W. P., & Wang, J. F. Synthesis and characterization of biodegradable and weather-durable PET/PEG/NDC copolymers. Colloid and Polymer Science, 290(14), 1381-1392 ,2012.

★★★