

CHAPTER IX
STRUCTURAL AND MECHANICAL RESPONSE OF POLY(ETHYLENE
TEREPHTHALATE)/LIQUID CRYSTALLINE POLYMER BLENDS TO
MICROWAVE RADIATION

9.1 Abstract

Poly(ethylene terephthalate) (PET) and its blend with 10 wt% liquid crystalline polymer, Vectra A950 (VA) were exposed to microwave energy up to 4 cycles. The observation was made on thermal, mechanical, and structural changes of the irradiated samples compared to the pristine ones. The dielectric heating caused by microwave exposure was found to induce cold crystallization, resulting in an increased degree of crystallinity for both PET and the blend. The VA component was the least sensitive to the microwave field yet it accelerated the crystallization process of the PET matrix. An improved tensile modulus and a decreased ductility were observed as a result of the increased crystalline extent for both samples. Tensile strength was found to improve only in the case of PET. The PET crystalline structure induced by microwave irradiation showed the same structure as that found from a typical thermal annealing. Therefore, the crystallization process of PET can be induced during microwave exposure without compromising the mechanical properties.

Key words: Crystallization; Liquid Crystalline Polymer; Microwave; Poly(ethylene terephthalate)

9.2 Introduction

The term 'Microwave' represents the electromagnetic radiation with frequencies ranging from 1- 300 GHz. One of the familiar applications is a domestic use

as a heat-generating source for processing food – the microwave oven. A microwave can also be utilized in telecommunications and material processing industries. Microwave technologies for processing materials are an alternative approach for improving material properties with the advantages of energy saving and reduced processing time. By microwave heating, a relatively uniform heat distribution throughout the samples could be achieved at once as contradictory to the conventional heating methods that rely on thermal conduction. A conventional microwave processing employs a fixed frequency, mostly at 2.45 GHz and 900 MHz to avoid interferences with telecommunication devices, although this use of a fixed frequency microwave might generate hot spots and thermal runaway. Examples of successful applications of this advanced technology reported are joining and welding polymer and polymer composites [1-4], processing of thermoplastics [5-8], vulcanizing rubber [9], and polymerization [10]. The factors involved in the microwave heating are the dielectric properties. A dielectric is an electrically insulating material placed between two parallel metallic plates. When an external, alternating field is applied, charges will be generated at the surface of a dielectric as a result of dipole reorientation. Since the dipoles are bound in the dielectric to some extent, forcing them to alternate can cause internal friction that has to be overcome. The energy from the microwave that is loss in this process is then converted into thermal energy leading to the localized heating of a dielectric. Polymeric materials can be considered as dielectrics as they are mostly non-conductive, consisting of polar molecules forming dipoles that are capable of oscillating under an applied alternating field. The internal friction caused by these oscillating dipoles lead to localized heating and is believed as a key mechanism for the dielectric heating of polymer [11]. One of the most important parameters of a dielectric material is the complex relative permittivity, ϵ , defined as follows:

$$\epsilon = \epsilon' - j\epsilon'' \quad (9.1)$$

where ϵ' is the real part of the permittivity, also called the dielectric constant. This parameter indicates how much the incident energy can enter the sample while the rest of the energy will be reflected at the air-sample interface.

The decisive factor determining how effectively the material can convert the incoming energy into heat is reflected through the loss tangent (also referred to as $\tan \delta$ or dielectric loss). A dielectric is a better absorber of the microwave energy if it exhibits a greater $\tan \delta$ value. This parameter is indicative of the phase lag between the dielectric field and the oscillating dipole and is expressed as;

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (9.2)$$

There are limited works utilizing the principle of dielectric heating through the application of a microwave to join polymers and polymer composites. This modern technology is still in its early development stage. Those polymers are acrylonitrile/butadiene/styrene [12], polymethylmethacrylate [12], polycarbonate [7,12], polyethylene [5], poly(ethylene terephthalate) [7], polyimide [7], nylon [5], and polyaniline [6]. Welding of polymer composites have been reported using various filler types, e.g. multi-walled carbon nanotube [6, 7], carbon black [13], zinc oxide [13], and talc [13]. To be fruitful, the systems chosen must absorb a sufficient amount of the microwave energy and convert it into heat such that welding with reasonable bond strength is achieved in a short amount of time.

In this contribution, we focused on the influence of microwave irradiation on a poly(ethylene terephthalate) (PET) and its blends with a liquid crystalline polymer, namely Vectra A950 (VA). These blends are also referred to as 'in-situ composites' as they exhibits properties similar to those of short-fiber reinforced composites but with the advantages of the improved processibility, light weight, and less abrasion of the processing facility. The temperature rise, structural, and mechanical properties of the samples were investigated.

9.3 Experimental

9.3.1 Materials

The Poly(ethylene terephthalate) (PET) was purchased from Indorama Polymers Public Company Limited, Thailand under the trade name RAMAPET N1. The LCP used was Vectra A950 (labeled VA hereafter), kindly supplied by Hoechst-Celanese. VA is a copolyester of 73 mol % p-hydroxybenzoic acid (HBA) and 27 mol % 2-hydroxy-6-naphthoic acid (HNA). The materials were dried in a vacuum oven at 130°C for 12 h before use.

9.3.2 Sample Preparation

PET and VA resins were premixed in a dry mixer to prepare VA/PET blends with a VA loading of 10 wt%, followed by melt-mixing in a self-wiping, co-rotating twin-screw extruder (Collin, ZX-25). The temperature of the barrel section from the feeding zone to the die was set at 95, 250, 260, 270, 275, 265°C. The rotor speed was controlled at 20 rpm. The extrudates were cooled by water and then pelletized. The pristine PET and PET/VA blend were shaped into a disc of 1 cm in diameter and 2 mm in thickness. They were in an amorphous state prior to microwave exposure. For the mechanical testing, the samples were injected at 260°C into dumbbell-shaped, 2.5 mm thick specimens using an AP-90 (Asian Plastic) injection molding machine and the mold temperature was kept low such that the amorphous samples could be achieved before being treated with a microwave.

9.3.3 Microwave Heating

Microwave irradiation was carried out using a domestic microwave oven (Samsung, M-183GN, 2.45 GHz, 850W). The sample was irradiated at 300 W from one to four cycles with each cycle lasting 20 min. During exposure, an infrared thermometer was used to detect the temperature of the sample as a function of time. After each cycle, the sample was taken out for the DSC characterization.

9.3.4 DSC Characterization

The thermal behaviors of the neat PET and PET/VA blends were analyzed using a Perkin-Elmer DSC7 differential scanning calorimeter (DSC). The instrument was calibrated with indium before the measurements were performed. The experiments started with heating each sample from 25°C to 300°C/min at a heating rate of 20°C/min under dry nitrogen atmosphere. The heat involved was then recorded as a function of temperature.

9.3.5 Determination of Mechanical Properties

Mechanical measurements were made in an Instron 4206 tensile tester at room temperature. The mechanical properties (tensile modulus, tensile strength, and elongation at break) were extracted from the stress–strain curves. The test conditions were set as follows: an extensional speed of 50 mm/min, an initial gauge length of 26 mm, and a load cell of 100 N. Test results were obtained by averaging the data from five samples.

9.3.6 Wide Angle X-ray Diffraction

Wide angle X-ray diffraction (WAXD) patterns were obtained from an X-ray diffractometer (XRD) (Bruker-AXS D8 Discover) using Ni filtered Cu K α radiation ($\lambda=154$ nm).

9.4 Results and Discussion

9.4.1 Temperature Profile of the Neat PET and the PET/VA Blend

Fig. 9.1 displays the temperature profile of PET, VA and their blend after being irradiated with the microwave energy. The data are fitted to a linear relationship using a least square method with an intention to draw a comparison and one should note that the loss factor actually depends on the temperature. Nonetheless, all the R-squared values obtained are greater than 0.97 implying only small influence of the sample

temperature on the loss factor in these samples. The slope of the regression line is used to infer how effectively the material can be heated via microwave irradiation. The values of the slope are reported in parentheses and the following trend is observed: PET (7.53) > PET/VA (5.65) > VA (4.33). At 1 MHz, the dissipation factor of PET is 0.0208 [14] and that of VA is 0.014 [15], while the dielectric constant of the former is 3.37 and the latter is 3.6. According to the definition of these two parameters, it can be concluded that both the materials can absorb the electromagnetic energy to a comparable extent but energy loss as heat is greater in PET than in VA. When introducing VA into PET, it is not surprising that the degree of temperature increase would fall in-between those of PET and VA. The slope value of the PET/VA blend is then less than PET but greater than VA.

9.4.2 Characterization of the Neat PET

9.4.2.1. *DSC characterization*

Fig. 9.2 depicts the DSC thermograms of the neat PET sample in an amorphous state (0 cycle) and the same sample after microwave exposure from 1 to 4 cycles. The glass transition is evident at approximately 50°C and is the clearest for an amorphous PET. After irradiation, the glass transition becomes less obvious indicating the decreasing amount of the amorphous fraction, yet no significant shift in the glass transition temperature is observed. The exotherms whose peak located at 150°C originates from the cold crystallization of PET during heating scan. PET has been reported to show double cold crystallization exotherms at 127 and 150°C belonging to the crystallization of interlamellar and interspherulitic regions respectively [16]. In this work, only the one at the higher temperature peak—the interspherulitic crystallization peak, is observed, owing to the low nucleation density as the starting sample is in an amorphous state. The cold crystallization peak disappears after 4 microwave cycles which implies the loss of crystallizable fraction. The extent of crystallization as calculated from the melting endotherm (peak maxima at 250°C), taking the heat of

fusion of fully crystalline PET of 117.6 J/g, is found to be 27% [17,18]. Microwave heating was then proven to be effective in inducing the cold crystallization in PET.

9.4.2.2. WAXD Patterns

The WAXD data from Fig. 9.3 clearly reveal an increase in the intensity of the crystalline scattering due to the increase in the crystallinity with increasing irradiation cycles. The X-ray peaks are associated to the triclinic phase [19] and in good agreement with data from the literature for PET. More specifically, the pattern of the diffractograms for samples treated with at least 2 cycles is similar to what reported for a PET cast film after thermal annealing in a thermo press [20] with the intensity much lower than what was found in PET crystallized from melt [21] suggesting the lower extent of PET crystallites obtained from cold-crystallization process. As there are no foreign peaks evident, it is deduced that the microwave exposure does not alter the crystalline structure of PET.

9.4.2.3. Mechanical Performance

Tensile test results for the neat PET with and without microwave exposure are shown in Table 9.1. The tensile modulus is found to increase with increasing microwave irradiation cycles. After 4 cycles, the tensile modulus of PET increases by 34% compared to the untreated one. The improved modulus can be ascribed to the increased crystallinity induced by microwave treatment as it is well known that crystallites have higher modulus than the amorphous fraction and they act as hard filler particles. Similarly, the slight improvement in the tensile strength caused by microwave irradiation is a result of these microwave-induced crystallites. These crystallites tie parts of polymer chains together causing the restriction in their motion in the similar manner to those due to cross-links [22,23]. As expected, with a greater degree of crystallinity, the percent elongation at break is drastically dropped.

9.4.3 Characterization of the PET/VA blend

9.4.3.1. DSC characterization

DSC heating thermograms of the PET/VA blends before and after microwave treatment are displayed in Fig. 9.4. Only the peaks belonging to PET component are observed since only 10 wt% of VA is used and the heat involved with the melting process of an LCP crystallites is usually small (2 J/g) [24]. The glass transition and the cold crystallization peaks are found only in the blend before microwave exposure. Therefore, it can be deduced that all the cold crystallization process is complete within one irradiation cycle. Further irradiation does not yield any significant changes to the degree of crystallinity as reflected through the comparable area under the melting peaks of the sample treated with various numbers of cycles (with $\pm 2\%$ error). The average normalized degree of crystallinity of PET/VA as induced by microwave treatment is found to be 34%, which is approximately 27% greater than what is observed in case of the neat PET. As a consequence, VA can promote PET cold crystallization process under microwave irradiation by increasing crystallization extent and accelerating the kinetics of the process. VA probably acts as a nucleating agent for PET cold crystallization. It has been reported that VA played the nucleating role in the melt crystallization process of PET [25, 26] and poly(trimethylene terephthalate) [27] as well.

9.4.3.2. WAXD Patterns

Shown in Fig. 9.5, is the diffraction pattern for PET/VA with and without microwave irradiation. The peak located at $2\theta = 19.98$ appears in all samples and corresponds to the HBA/HNA copolymers VA structural units [28-30]. The other peaks obviously belong to the PET component and they present consistency in their locations regardless of the number of microwave cycles. The similar conclusion to that of PET then can be drawn; microwave irradiation does not have influences on the crystalline structure of the PET component.

9.4.3.3. Mechanical Performance

The mechanical properties for the PET/VA blend are shown in Table 9.2. A slight improvement in the tensile modulus is found after one microwave cycle. With further microwave treatment the values start to level off. This can be explained based on the DSC results that the cold crystallization process ceases after one

irradiation cycle resulting in no more crystalline formation that could further raise the modulus. The tensile strength is less affected than the modulus and the standard deviation values make it difficult to evaluate the effects of microwave irradiation on the ultimate strength of the blend. It might be stated that the tensile strength is not significantly changed by the microwave radiation. The percent elongation at breaks are all comparable for every sample despite the microwave treatment since introducing VA already decreased the ductility of the system to a very low value.

9.5 Conclusions

The concept of a dielectric heating through microwave irradiation was applied to the neat PET and the PET blend with 10 wt% liquid crystalline polymer. The structural, thermal and mechanical properties were investigated. VA showed the least sensitivity to microwave treatment as its temperature increased at the slowest rate, whereas PET exhibited the greatest sensitivity and the PET/VA blend fell in-between. It was found that microwave irradiation induced cold crystallization process of both the neat polymer and the blend, with stronger effects on the latter in terms of crystallization kinetics, signifying that VA functioned as a nucleating agent. An increase in the crystallization extent rendered better tensile modulus for both samples but the effects on the tensile strength and ductility were less pronounced for the blend than the neat PET. XRD results indicated no alteration of the PET crystalline structure compared to that of the thermally annealed PET.

9.6 Acknowledgements

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9.7 References

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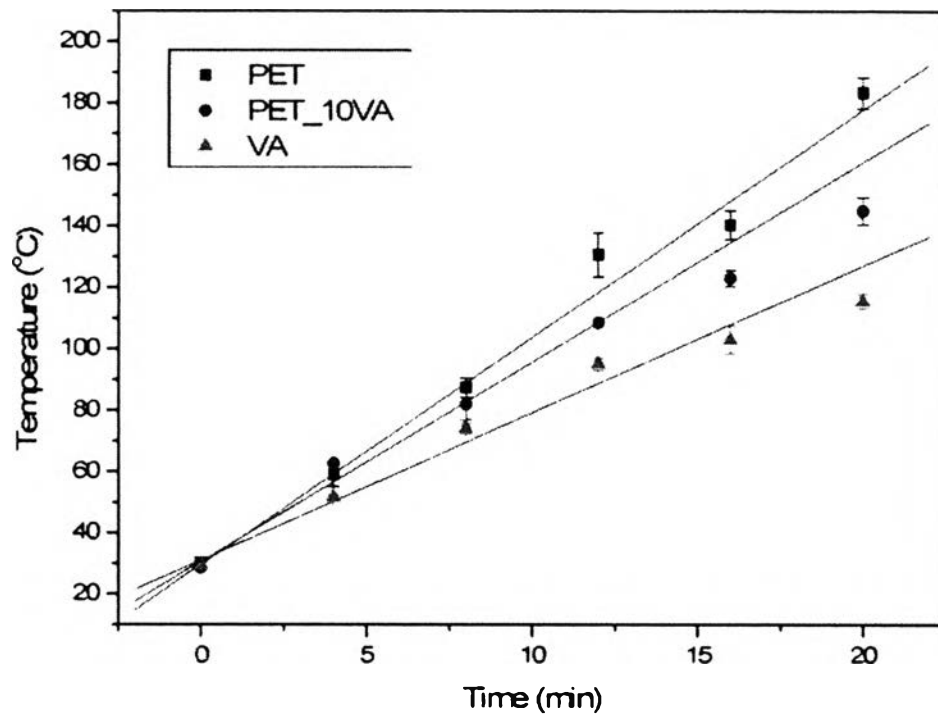


Figure 9.1 Sample temperature as a function of time during microwave heating.

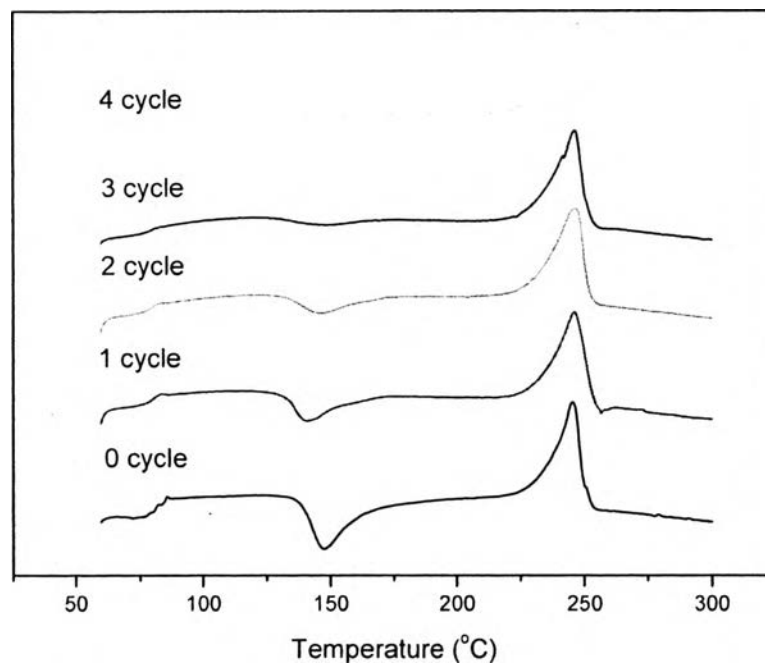


Figure 9.2 DSC heating scans of the neat PET samples after various cycles of microwave irradiation.

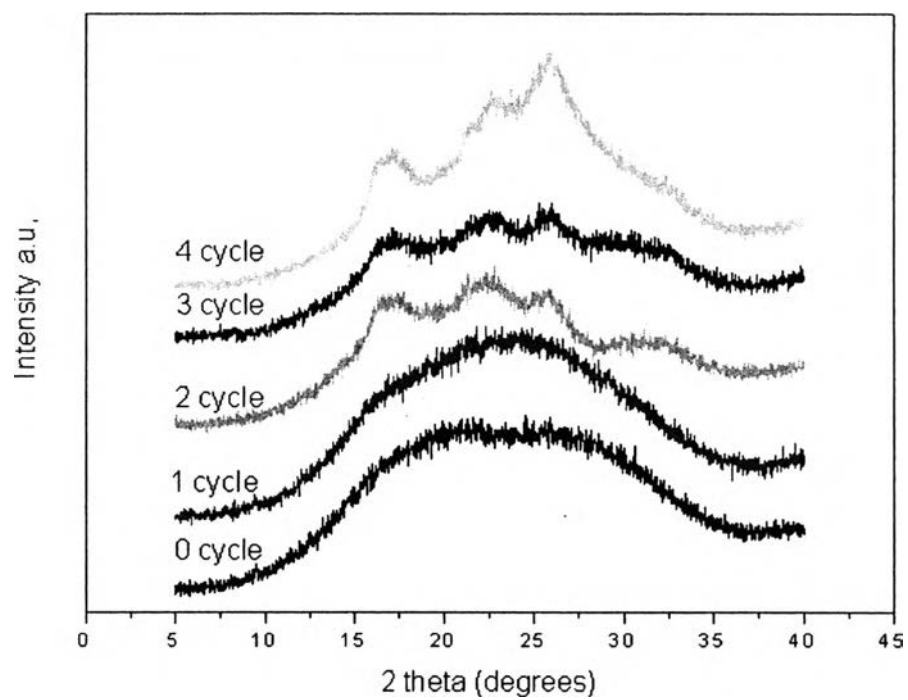


Figure 9.3 X-ray diffractograms of the PET before and after microwave irradiation at different numbers of cycles.

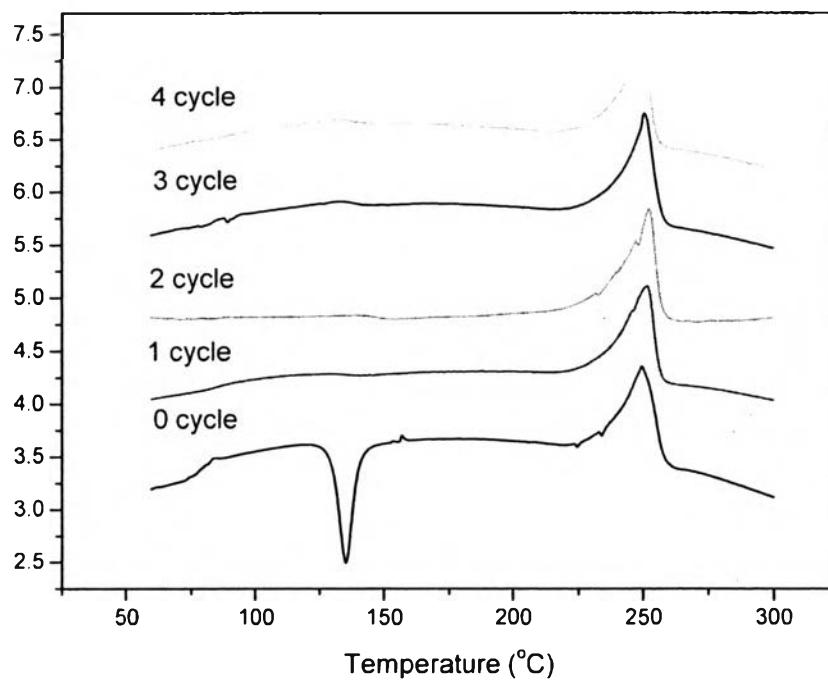


Figure 9.4 DSC heating scans of the neat PET samples after various cycles of microwave irradiation.

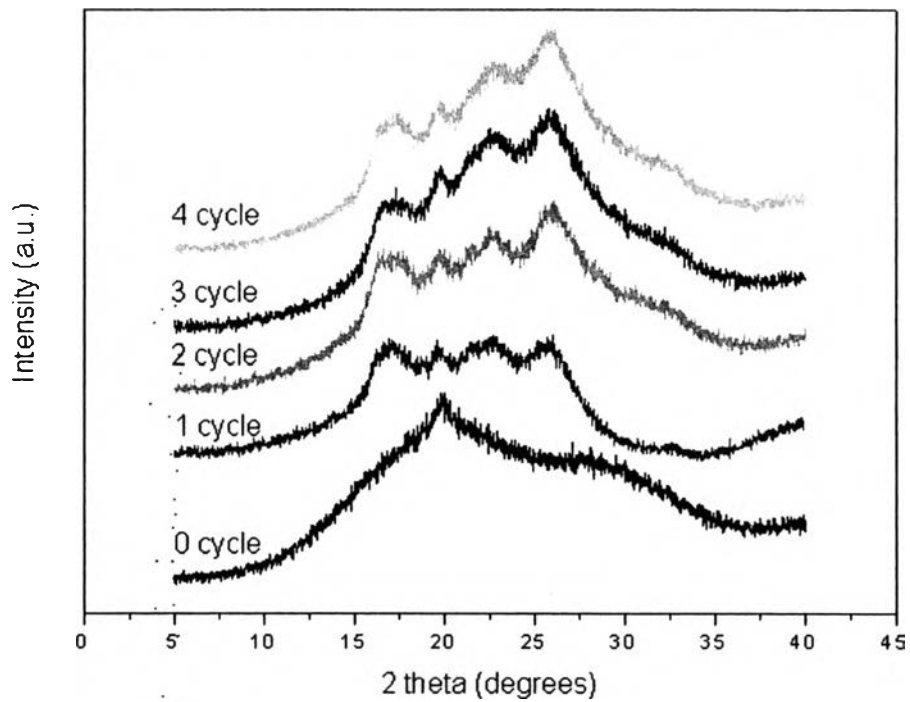


Figure 9.5 X-ray diffractograms of PET/VA blends before and after microwave irradiation at different number of cycles.

Table 9.1 The static mechanical properties of PET

No. of cycle	Tensile Modulus (MPa)	Tensile Strength (MPa)	% elongation at break
0	1201.8 (39.6)	62.9 (5.2)	563.4 (0.6)
1	1571.0 (35.6)	72.4 (2.6)	40.6 (2.9)
2	1582.8 (125.7)	74.0 (2.1)	40.0 (11.2)
3	1549.7 (103.8)	71.5 (2.8)	51.0 (25.0)
4	1613.0 (49.5)	70.7 (3.2)	35.0 (18.0)

Note: The standard deviation values were shown in parenthesis

Table 9.2 The static mechanical properties of PET /10VA

No. of cycle	Tensile Modulus (MPa)	Tensile Strength (MPa)	%elongation at break
0	1638.4 (16.7)	63.7 (3.6)	5.0 (0.5)
1	1772.0 (64.2)	66.3 (4.4)	4.8 (0.6)
2	1848.2 (105.0)	65.1 (7.1)	4.6 (0.9)
3	1789.3 (79.9)	69.1 (3.2)	5.1 (0.7)
4	1759.3 (69.4)	67.6 (3.4)	5.2 (1.2)

Note: The standard deviation values were shown in parenthesis