# CHAPTER IV
# DEGRADATION OF PLASTIC CARDS

## 4.1 Abstract

A number of commercial plastic card materials, such as polyvinyl chloride (unplasticized) (PVC), polycarbonate (PC) and polyethylene terephthalate glycol (PETG), are widely used as smart card body. Usually, the degradation of plastic materials is concerned because the life time of smart card is required to specify. The study of plastic cards degradation by moisture, light, and temperature with outdoor exposure and accelerated weathering test in Thailand has never been studied. Therefore, this study aims to correlate the outdoor exposure condition with the condition in accelerated weathering tester or QUV. The outdoor exposure periods were set at 1, 2, 3, 4, 5, and 6 months. Accelerated weathering test was performed by QUV accelerated weathering tester. The correlation was justified by mechanical, physical and thermal properties. Total color different ($\Delta E$) and gloss at 60° of plastic cards results showed that surface of plastic card were degraded by effect the of exposure. The longer exposure time the higher degradation. Mechanical property was investigated by Young's modulus tensile strength and toughness. The mechanical property's results show that the PC has the highest strength and PVC has the highest stiffness. The accelerated weathering tester helped to determine the periods of time when plastic cards were degraded. The outdoor exposure deteriorated plastic cards more severe than QUV accelerated weathering tester. Plastic cards were sallow and brittle when exposed to the UV for long periods of time. The largest degradation in both outdoor exposure and QUV accelerated weathering tester was exhibited in PVC cards.

## 4.2 Introduction

Undeniable, consumption of smart card in Thailand is increased rapidly such as identification card, credit card and souvenir. Smart card was a higher level of security, easy to carry them around and easy to use them (J. Markarian, 2004).

Materials of smart card body were either commodity plastics such as Polyvinyl Chloride (PVC) and Polyethylene Terephthalate Glycol (PETG) or engineering plastics such as Acrylonitrile Butadiene Styrene (ABS) and Polycarbonate (PC). PVC is an amorphous thermoplastic material. The property of unplasticizer PVC is colorless and rigid. PC is a polyester type and amorphous structure. PC properties are transparency, rigidity, substantial heat resistance, acid resistance (but not against alkalis), and good impact durability. PETG is amorphous co-polyester. PETG are flexible in processing, non-toxie and environmental friendly (R. Wolfgang *et al.*, 2004).

Study in reduction of service lifetime is important for increasing value of a product. The cause of deterioration of the materials when use in outdoor condition is much affect by environment. There are two experiment one, that was weathering accelerated by QUV accelerated weathering tester and another was exposure outdoor. Accelerated weathering tester is often used in experiment because exposure hours of accelerated weathering tester help to compute years of outdoor exposure. The results used to predict service life outdoor or in the in-service environment. But the problem is the inherent variability and complexity of outdoor exposure situations.

The objectives of this study are to observe the effect of environment on plastic cards in mechanical properties, physical properties and thermal properties. and to study the correlation between the degradation in accelerated weathering exposure and outdoor exposure of the plastic card body (PVC, PC and PETG).

## 4.3 Experimental

Accelerated weathering test was measured by QUV accelerated weathering tester. QUV accelerated weathering tester was used with UV-B lamps irradiance at 0.48 W/m$^2$ 340 nm. for 4 hours at 37°C and dark light under condensation for 4 hours at 37°C.

The outdoor exposure testing periods were set at 1, 2, 3, 4, 5 and 6 months. Samples were exposed in Bangkok's weather.

## 4.4 Results and Discussions

The plastic card properties were compared between each material in QUV accelerated weathering tester and outdoor exposure. From visual inspection, all samples were yellowing and less glossy.

### 4.4.1 Haze-Gloss Testing

The ability of materials to resist color change was only part of the necessary performance parameters. The results were also essential that the surface did not chalk but loss of gloss at 60°. In QUV accelerated weathering tester conditions PVC, PC and PETG cards changed -9.57%, -2.14% and -6.03% respectively. In outdoor exposure conditions PVC, PC and PETG cards changed -13.85%, -4.32% and -4.21% respectively.

**Table 4.1** The average gloss value at 60° of plastic cards after exposure in QUV accelerated weathering tester

| Condition | The average gloss value at 60° | | |
|---|---|---|---|
| | **PVC** | **PETG** | **PC** |
| Non exposure | 92.70±0.26 | 97.20±0.69 | 102.80±1.40 |
| QUV 1 cycle | 90.71±1.14 | 97.72±0.78 | 100.36±1.36 |
| QUV 3 cycles | 90.50±1.21 | 96.80±0.79 | 99.30±1.84 |
| QUV 6 cycles | 88.80±1.04 | 95.70±1.63 | 103.00±1.06 |
| QUV 9 cycles | 84.14±1.05 | 94.84±3.05 | 101.20±2.10 |
| QUV 12 cycles | 87.05±1.28 | 92.21±2.75 | 101.02±1.49 |
| QUV 15 cycles | 83.83±1.27 | 91.34±2.56 | 100.60±1.00 |

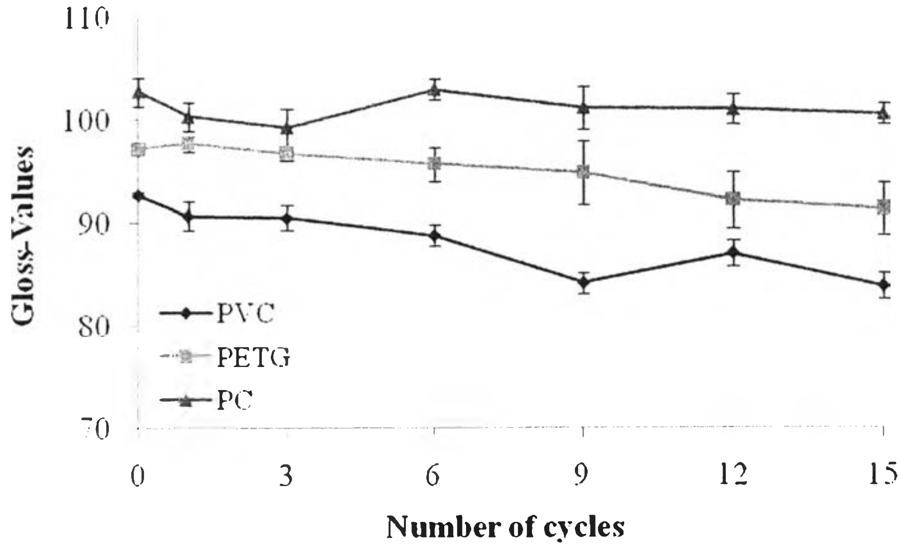


**Figure 4.1** The average gloss value at 60° of plastic cards after exposure in QUV accelerated weathering tester.

**Table 4.2** The average gloss value at 60° of plastic cards after outdoor exposure

| Condition | The average gloss value at 60° | | |
|---|---|---|---|
| | **PVC** | **PETG** | **PC** |
| Non exposure | 92.70±0.26 | 97.20±0.69 | 102.80±1.40 |
| Outdoor 1 month | 85.90±1.95 | 97.10±0.89 | 102.30±0.74 |
| Outdoor 2 months | 81.28±1.46 | 94.34±4.52 | 96.79±2.54 |
| Outdoor 3 months | 83.26±2.13 | 96.62±2.17 | 99.86±1.66 |
| Outdoor 4 months | 81.96±2.04 | 96.58±1.22 | 100.18±1.94 |
| Outdoor 5 months | 81.80±2.05 | 94.91±3.53 | 99.25±1.47 |
| Outdoor 6 months | 79.86±3.23 | 93.11±2.24 | 98.25±1.95 |

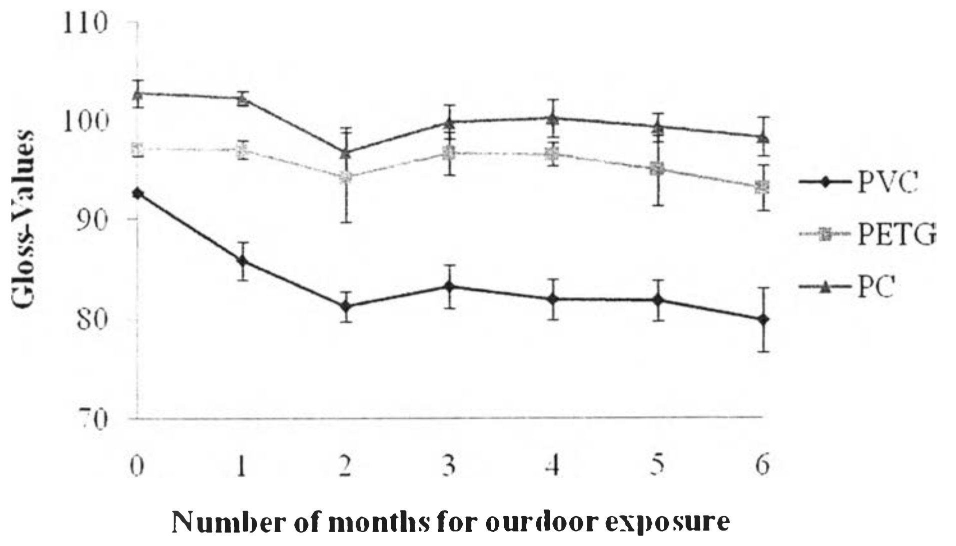


**Figure 4.2** The average gloss value at 60° of plastic cards after outdoor exposure.

4.4.2 Colorimetric Spectrophotometer analysis

From the result of total color different (ΔE), ΔE was found to increase for all materials. In QUV accelerated weathering tester condition, ΔE of PVC, PC and PETG cards changed 36.77, 32.04 and 23.14 units respectively (Table 4.3). In outdoor condition, ΔE of PVC, PC and PETG cards changed 55.89, 20.40 and 19.31 units respectively (Table 4.4). PVC was highly changed in both conditions because PVC sequences have more conjugated double bonds that were chromophores and gave rise to the family yellowing and discoloration, which formed when PVC heated (C. E. Wilkes *et al.,* 2005). PC and PETG become yellow because degradation processes: photo-Fries rearrangement and fragmentation (D. Bellus *et al.*, 1966), (J. S. Humphrey Jr *et al.,* 1973), (D. G. Legrand *et al.*, 2000), (J. R. Fried *et al.*, 2003), side chain oxidation (A. Factor *et al.*, 1980), (J. R. Fried *et al.*, 2003) and ring oxidation. Resent spectral studied by Lamaire and coworker (J. Lemaire *et al.*, 1983), (J. Lemaire *et al.*, 1986) and Pryde (C. A. Pryde, 1985) clearly illustrate that photo-Fries reactions were favored when light with $\lambda \leq 300$ nm was used, whereas photooxidation reactions were increasingly important as UV light of longer wavelength was used. Furthermore, all sample trended upward for the duration of the test.

**Table 4.3** The average total color different of plastic cards after exposure in QUV accelerated weathering tester

| Condition | The average total color different (ΔE) | | |
|---|---|---|---|
| | **PVC** | **PETG** | **PC** |
| QUV 1 cycle | 6.02±0.31 | 3.74±0.23 | 4.81±0.19 |
| QUV 3 cycles | 7.48±0.48 | 4.36±0.11 | 8.38±0.34 |
| QUV 6 cycles | 12.72±0.95 | 6.36±0.32 | 12.89±0.46 |
| QUV 9 cycles | 19.75±0.45 | 7.60±0.23 | 16.72±0.83 |
| QUV 12 cycles | 20.64±0.63 | 8.30±0.22 | 18.94±0.55 |
| QUV 15 cycles | 36.77±0.32 | 23.14±0.27 | 32.04±0.38 |

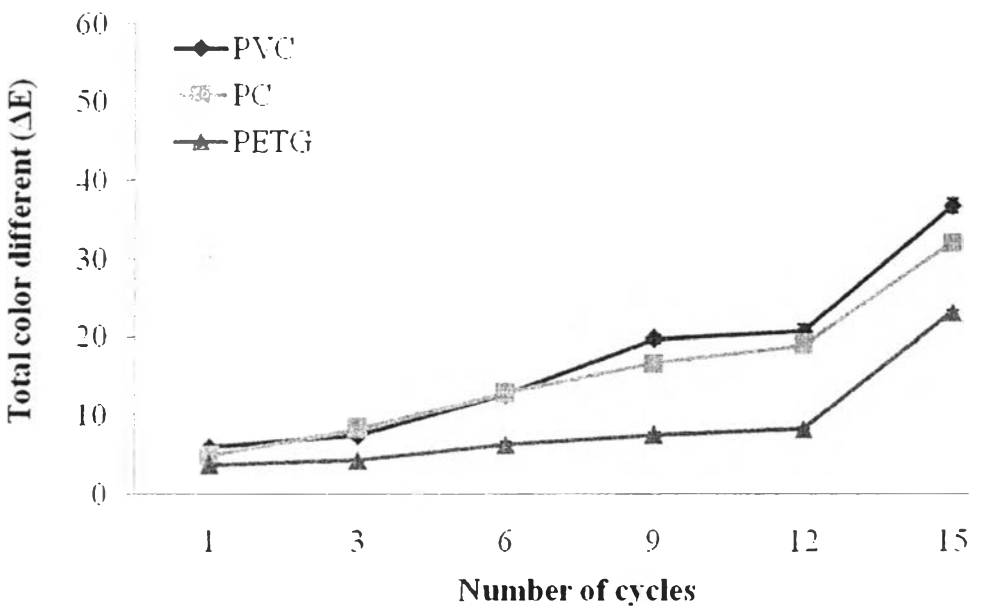


**Figure 4.3** The average total color different of plastic cards after exposure in QUV accelerated weathering tester.

**Table 4.4** The average total color different of plastic cards after outdoor exposure

| Condition | The average total color different (ΔE) | | |
|---|---|---|---|
| | **PVC** | **PETG** | **PC** |
| Outdoor 1 months | 28.78±0.96 | 2.28±0.16 | 1.12±0.15 |
| Outdoor 2 months | 31.30±0.96 | 3.35±0.22 | 2.21±0.17 |
| Outdoor 3 months | 38.06±0.68 | 4.51±0.09 | 3.76±0.17 |
| Outdoor 4 months | 47.40±0.91 | 5.56±0.20 | 4.99±0.23 |
| Outdoor 5 months | 45.07±1.33 | 5.80±0.25 | 5.23±0.22 |
| Outdoor 6 months | 55.89±9.94 | 19.31±0.43 | 20.40±0.29 |

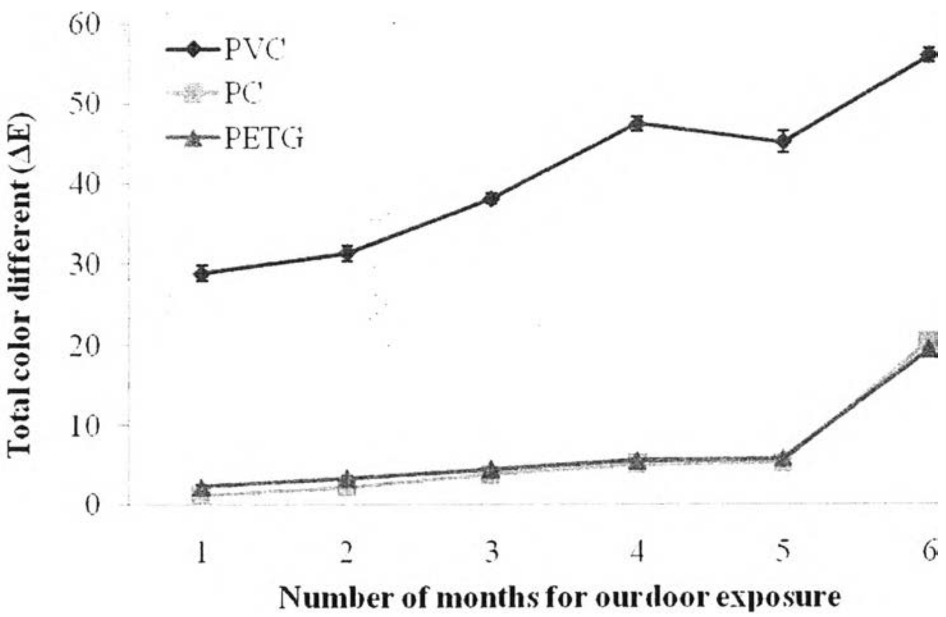


**Figure 4.4** The average total color different of plastic cards after outdoor exposure.

4.4.3 Tensile Property Testing

Young's modulus, tensile strength and toughness of samples were exhibited in Table 4.5, 4.6, 4.7, 4.8, 4.9 and 4.10. The average Young's modulus of PVC, PC and PETG cards after exposure in QUV accelerated weathering tester have trend to increase (Figure 4.5). The average Young's modulus in outdoor condition of

PVC, PC and PETG cards have trend to decrease (Figure 4.6). The average tensile strength of PVC, PC and PETG cards after exposure in QUV accelerated weathering tester decreased 11.26%, 6.26%, and 11.69% respectively. The average tensile strength of PVC, PC and PETG cards after outdoor exposure was lower by changed 47.12%, 5.32%, and 38.19% respectively. The average toughness of PVC, PC and PETG cards after exposure in QUV accelerated weathering tester lower changed 98.34%, 90.69%, and 81.76% respectively. The average toughness of PVC, PC and PETG cards after outdoor exposure lower changed 99.54%, 77.22, and 90.76 respectively.

The results indicated that after 15 cycles in QUV accelerated weathering tester, all plastics cards show insignificantly change of tensile strength. Comparing those with tensile strength measurement after outdoor exposure, all plastics cards show large dropped of tensile strength and more brittleness. And the higher degradation was found in PVC card because PVC exhibited the highest elastic deformation among those 3 plastics under the applied force. Tensile strength of all materials in outdoor exposure tested trended downward for the duration of the test. But in QUV accelerated weathering tested, the tensile strength were also stabled and remained constant for the duration. Another cause to changing of mechanical properties was dislocation occurred in the structure.

**Table 4.5** The average Young's modulus of plastic cards after exposure in QUV accelerated weathering tester

| Condition | The average Young's modulus (MPa) | | |
|---|---|---|---|
| | PVC | PETG | PC |
| Non exposure | 1330.20±132.69 | 1064.60±58.24 | 1184.40±84.82 |
| QUV 1 cycle | 1137.20±43.92 | 1401.80±95.22 | 1495.60±64.12 |
| QUV 3 cycles | 1144.60±116.42 | 1111.00±43.90 | 1093.00±62.01 |
| QUV 6 cycles | 1310.20±67.15 | 1143.00±45.81 | 1277.60±81.52 |
| QUV 9 cycles | 1336.00±89.88 | 1201.20±30.58 | 1295.60±78.21 |
| QUV 12 cycles | 1393.80±125.37 | 1215.60±97.09 | 1290.80±109.57 |
| QUV 15 cycles | 1383.40±100.69 | 1159.60±73.45 | 1383.40±143.13 |

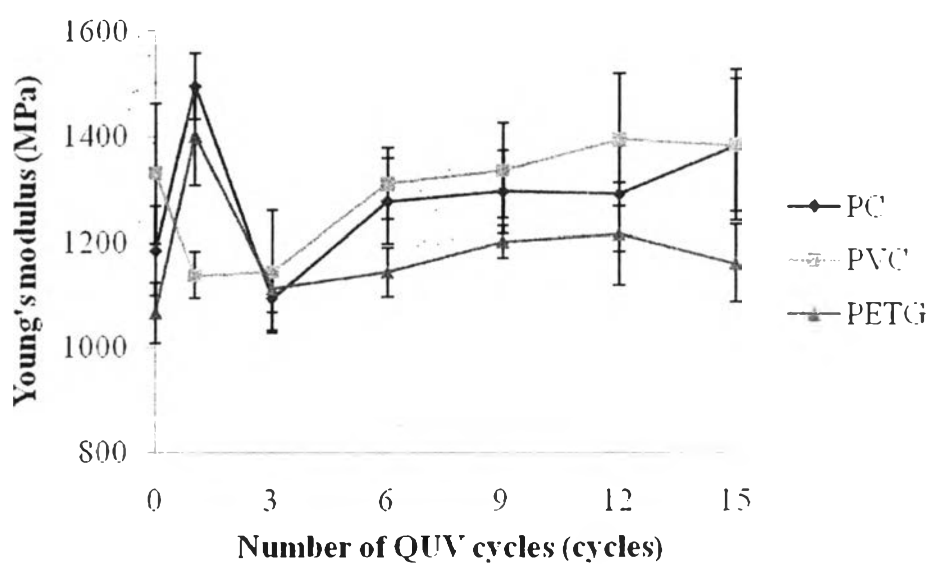


**Figure 4.5** The average Young's modulus of plastic cards after exposure in QUV accelerated weathering tester.

**Table 4.6** The average Young's modulus of plastic cards after outdoor exposure

| Condition | The average Young's modulus (MPa) | | |
|---|---|---|---|
| | PVC | PETG | PC |
| Non exposure | 1330.20±132.69 | 1064.60±58.24 | 1184.40±84.82 |
| Outdoor 1 month | 1256.40±52.90 | 1063.00±33.90 | 1227.80±32.77 |
| Outdoor 2 months | 1466.80±120.74 | 1200.60±40.67 | 1381.40±130.62 |
| Outdoor 3 months | 1381.60±86.69 | 1064.80±84.19 | 1177.80±131.68 |
| Outdoor 4 months | 1351.00±122.95 | 1007.80±67.02 | 1155.60±108.95 |
| Outdoor 5 months | 1326.00±91.32 | 995.60±47.19 | 1251.80±85.54 |
| Outdoor 6 months | 1183.20±100.69 | 969.80±81.14 | 1199.00±76.83 |

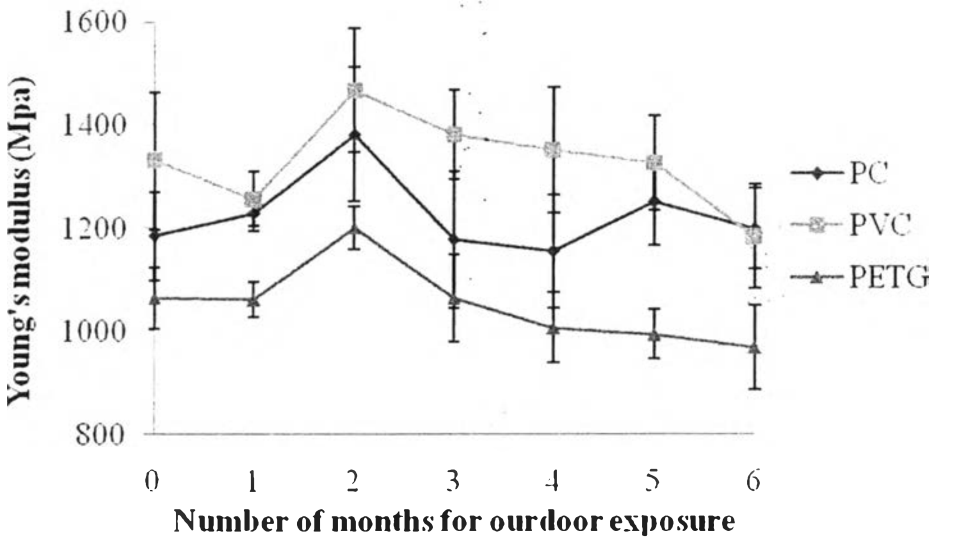


**Figure 4.6** The average Young's modulus of plastic cards after outdoor exposure.

**Table 4.7** The average tensile strength of plastic cards after exposure in QUV accelerated weathering tester

| Condition | The average tensile strength (GPa) | | |
|---|---|---|---|
| | **PVC** | **PETG** | **PC** |
| Non exposure | 53.28±2.67 | 50.83±2.60 | 70.30±2.42 |
| QUV 1 cycle | 48.49±1.82 | 67.23±3.42 | 56.73±1.59 |
| QUV 3 cycles | 47.81±2.21 | 49.41±1.58 | 63.12±0.60 |
| QUV 6 cycles | 47.26±2.79 | 46.79±2.39 | 64.77±1.48 |
| QUV 9 cycles | 51.44±1.59 | 48.95±3.67 | 62.79±2.25 |
| QUV 12 cycles | 55.28±2.09 | 49.89±2.70 | 66.70±4.94 |
| QUV 15 cycles | 47.28±3.11 | 44.89±8.26 | 65.90±2.33 |

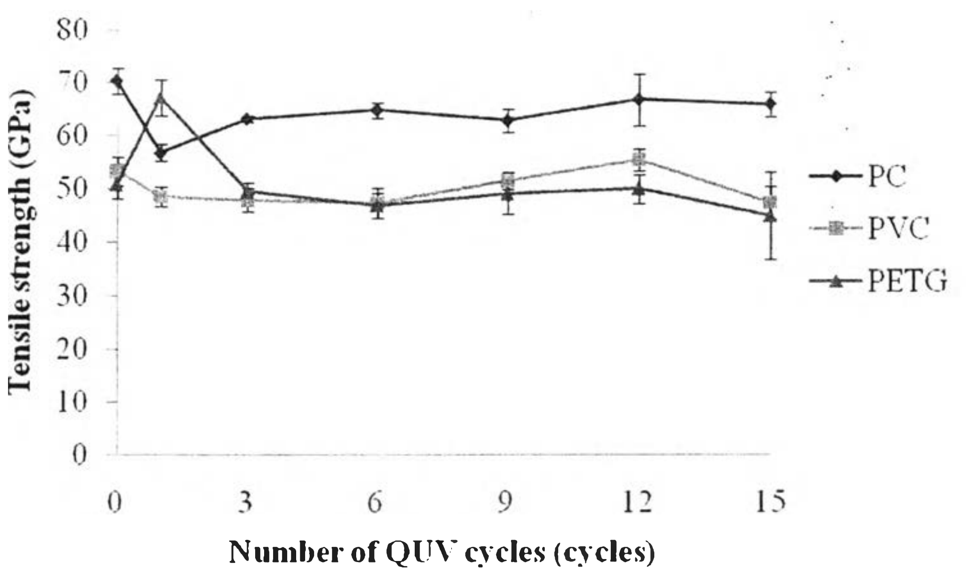


**Figure 4.7** The average tensile strength of plastic cards after exposure in QUV accelerated weathering tester.

**Table 4.8** The average tensile strength of plastic cards after outdoor exposure

| Condition | The average tensile strength (GPa) | | |
|---|---|---|---|
| | PVC | PETG | PC |
| Non exposure | 53.28±2.67 | 50.83±2.60 | 70.30±2.42 |
| Outdoor 1 month | 46.92±5.51 | 50.52±1.58 | 64.10±5.51 |
| Outdoor 2 months | 39.66±6.62 | 43.37±8.82 | 72.25±6.62 |
| Outdoor 3 months | 36.81±5.25 | 34.42±2.16 | 64.80±5.25 |
| Outdoor 4 months | 34.77±4.74 | 28.85±3.97 | 63.49±4.27 |
| Outdoor 5 months | 32.59±5.40 | 27.50±3.69 | 65.41±1.91 |
| Outdoor 6 months | 27.75±4.93 | 31.42±5.00 | 66.56±1.87 |

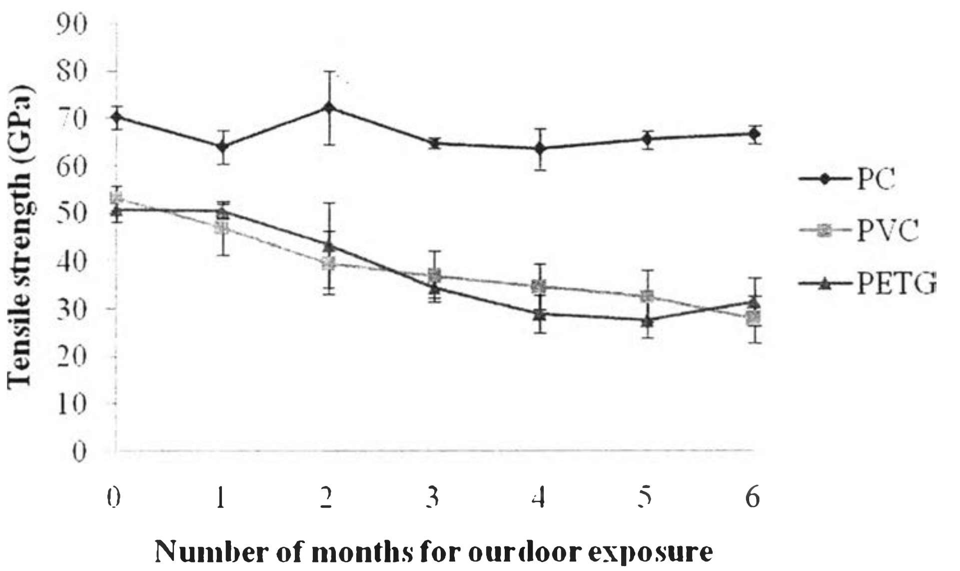


**Figure 4.8** The average tensile strength of plastic cards after outdoor exposure.

**Table 4.9** The average toughness of plastic cards after exposure in QUV accelerated weathering tester

| Condition | The average toughness (Mpa) | | |
|---|---|---|---|
| | PVC | PETG | PC |
| Non exposure | 84.37±2.95 | 8.66±1.53 | 51.97±9.99 |
| QUV 1 cycle | 76.87±2.28 | 10.59±3.57 | 14.64±7.77 |
| QUV 3 cycles | 14.98±5.87 | 5.01±3.31 | 16.18±3.41 |
| QUV 6 cycles | 3.74±0.80 | 1.79±0.15 | 13.35±1.96 |
| QUV 9 cycles | 2.71±0.30 | 2.34±0.68 | 11.64±4.86 |
| QUV 12 cycles | 3.25±0.55 | 1.83±0.07 | 5.91±2.96 |
| QUV 15 cycles | 1.40±0.31 | 1.58±0.37 | 4.84±1.33 |

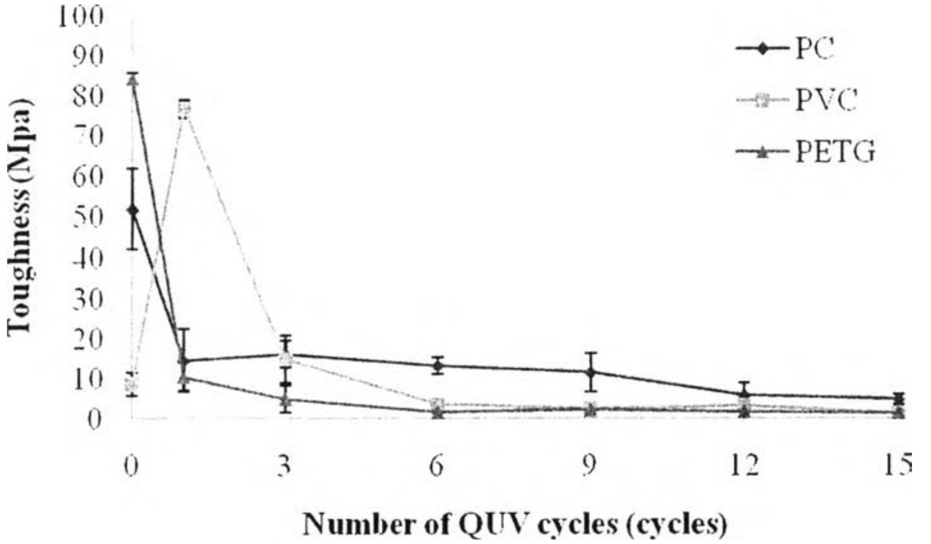


**Figure 4.9** The average toughness of plastic cards after exposure in QUV accelerated weathering tester.

**Table 4.10** The average toughness of plastic cards after outdoor exposure

| Condition | The average toughness (Mpa) | | |
|---|---|---|---|
| | PVC | PETG | PC |
| Non exposure | 84.37±1.53 | 8.66±2.95 | 51.97±9.99 |
| Outdoor 1 month | 1.58±0.66 | 2.20±0.17 | 14.00±2.48 |
| Outdoor 2 months | 0.80±0.24 | 1.90±0.58 | 17.84±3.53 |
| Outdoor 3 months | 0.65±0.20 | 0.98±0.06 | 19.73±5.41 |
| Outdoor 4 months | 0.56±0.14 | 0.72±0.36 | 13.04±4.84 |
| Outdoor 5 months | 0.54±0.18 | 0.73±0.43 | 12.29±6.91 |
| Outdoor 6 months | 0.39±0.12 | 0.80±0.31 | 11.84±2.74 |

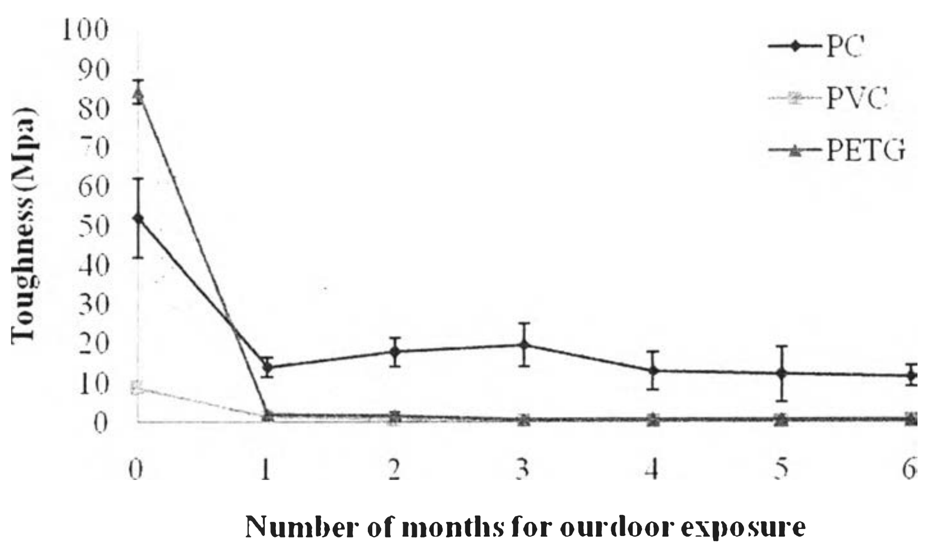


**Figure 4.10** The average toughness of plastic cards after outdoor exposure.

4.4.4 Thermal stability

The degradation temperature of PC card was higher than PETG and PVC card and % weight loss of PC was also found to be lower than that PETG and PVC. Hence, PC was much more stable at the same operating temperature.

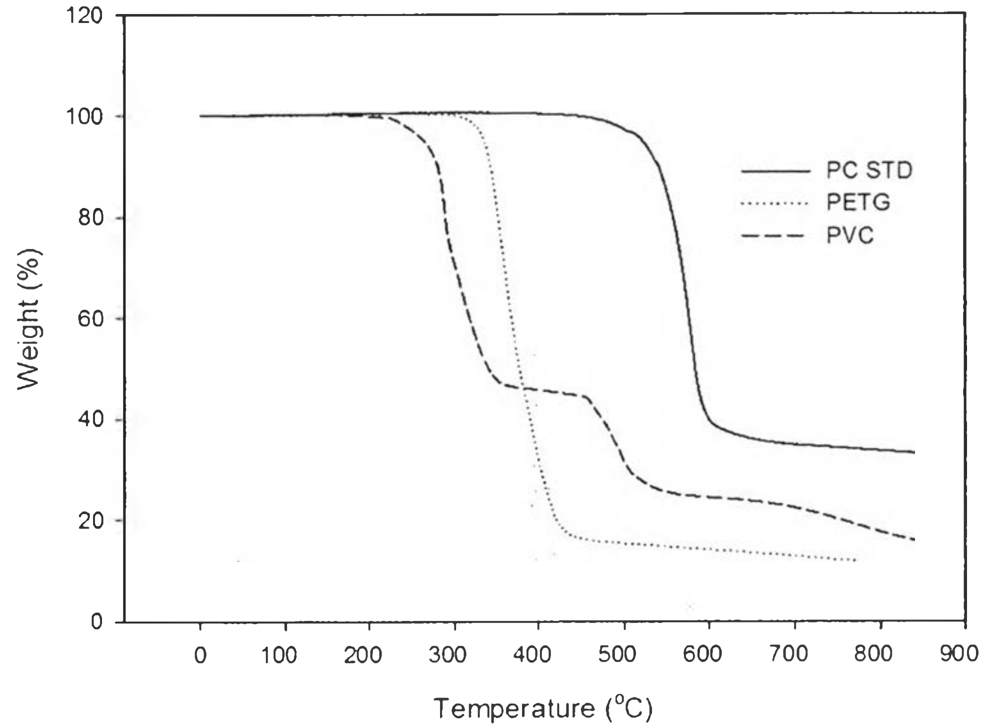


**Figure 4.11** TGA plots of plastic card.

**Table 4.11** $T_d$ degradation content (weight loss) of plastic card

| **Materials** | **$T_d$ (°C)** | **Weight loss (%)** |
|---|---|---|
| PC | 500.10 | 65.90 |
| PETG | 383.80 | 87.00 |
| PVC | 281.80 and 437.60 | 53.90 and 21.90 |

4.4.5 Topography

AFM measurements performed in non-contact mode revealed that the surface of plastic cards was smooth and no significant differences in topography. Three-dimensional profiles of the outdoor exposure sample surfaces were rougher than the sample after exposure in QUV accelerated weathering tester.

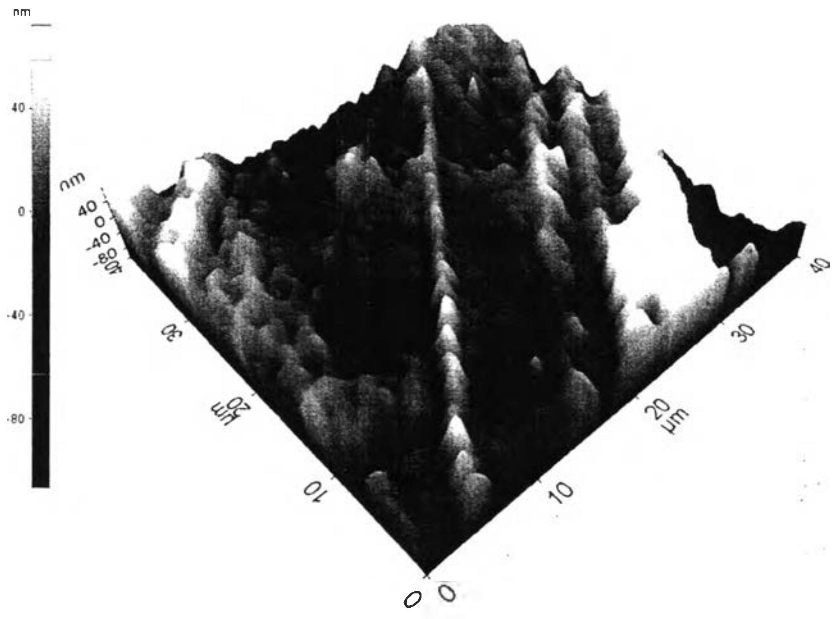


**Figure 4.12** Typical topography in 3D-profiles of the surfaces of PVC cards before exposure.

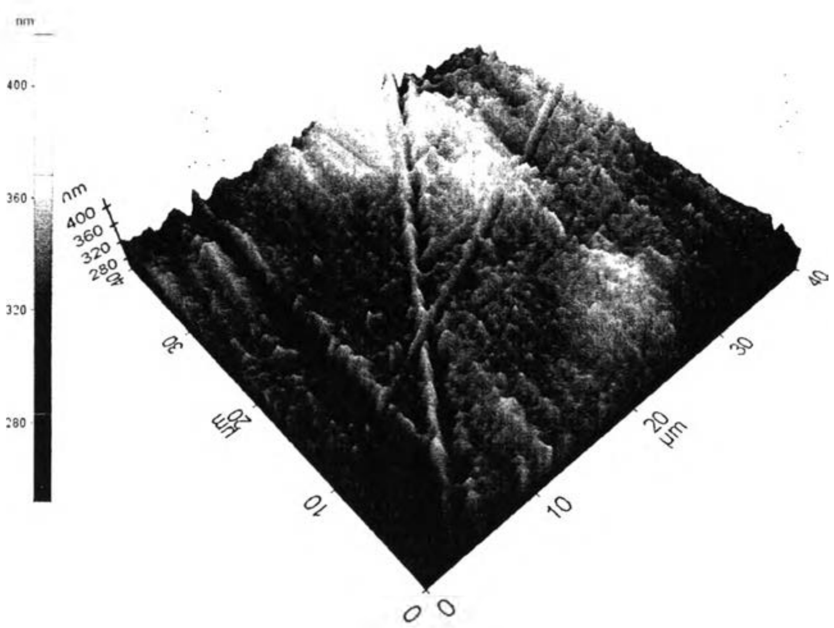


**Figure 4.13** Typical topography in 3D-profiles of the surfaces of PVC cards after exposure in QUV accelerated weathering tester for 15 cycles.

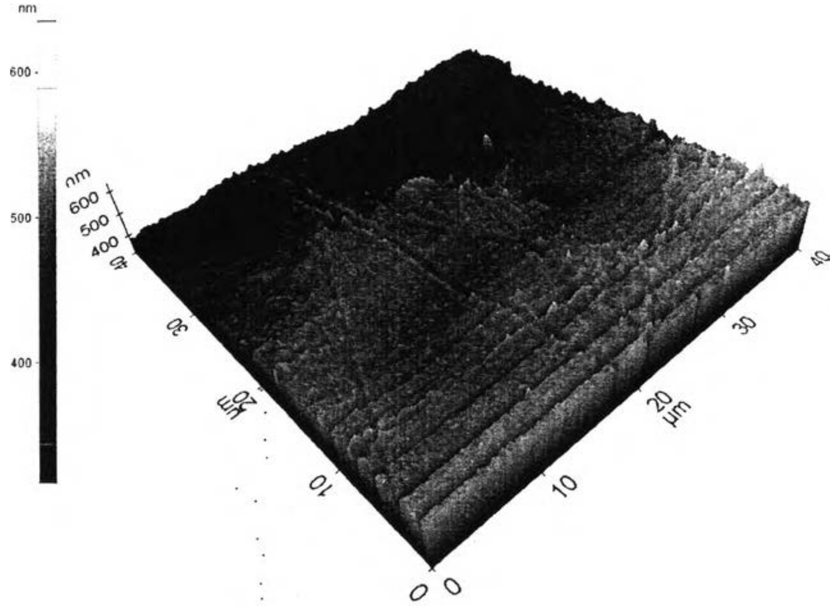


**Figure 4.14** Typical topography in 3D-profiles of the surfaces of PVC cards after outdoor exposure for 5 months.

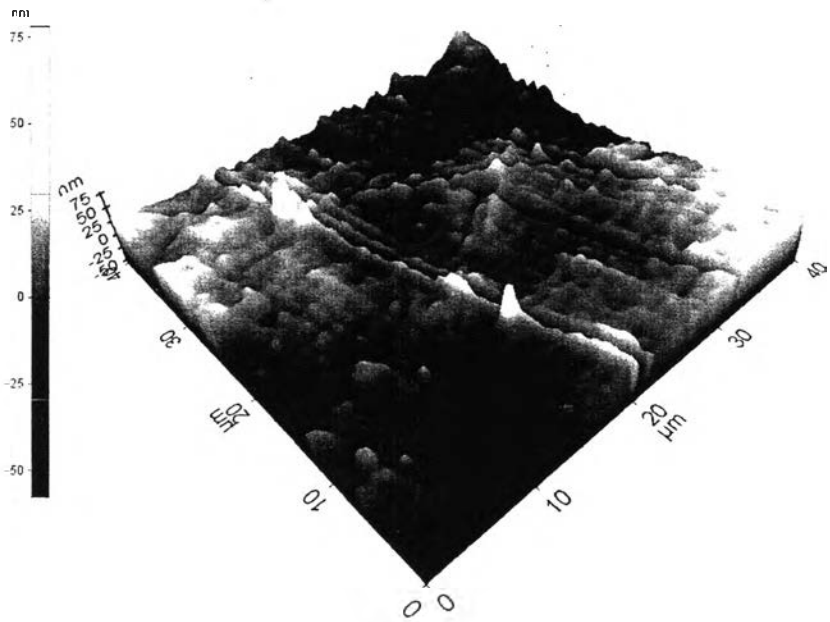


**Figure 4.15** Typical topography in 3D-profiles of the surfaces of PC cards before exposure.

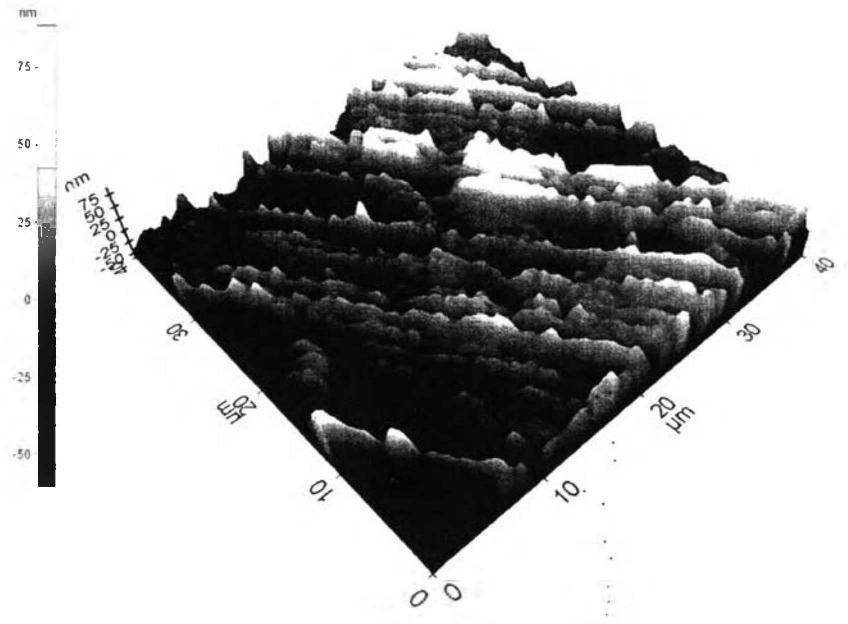

**Figure 4.16** Typical topography in 3D-profiles of the surfaces of PC cards after exposure in QUV accelerated weathering tester for 15 cycles.

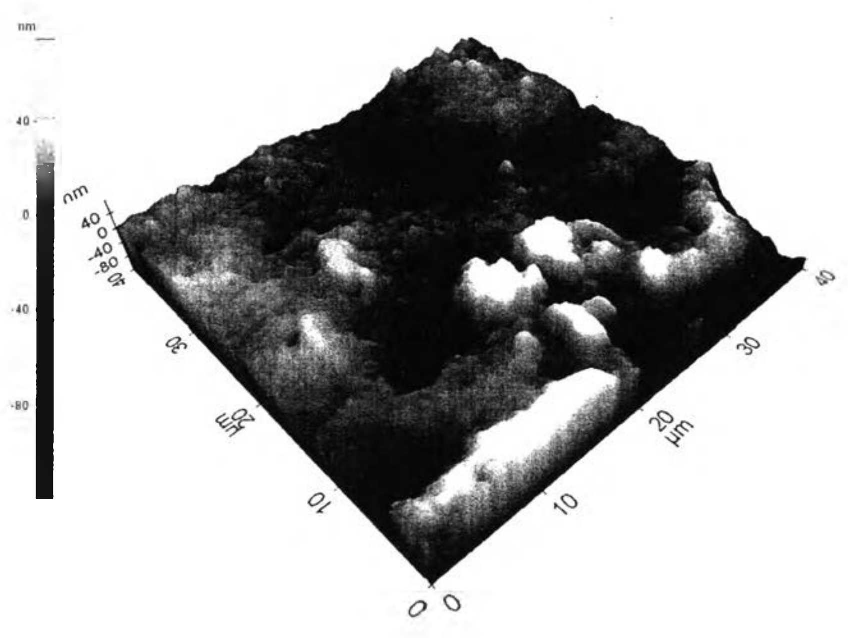

**Figure 4.17** Typical topography in 3D-profiles of the surfaces of PC cards after outdoor exposure for 5 months.

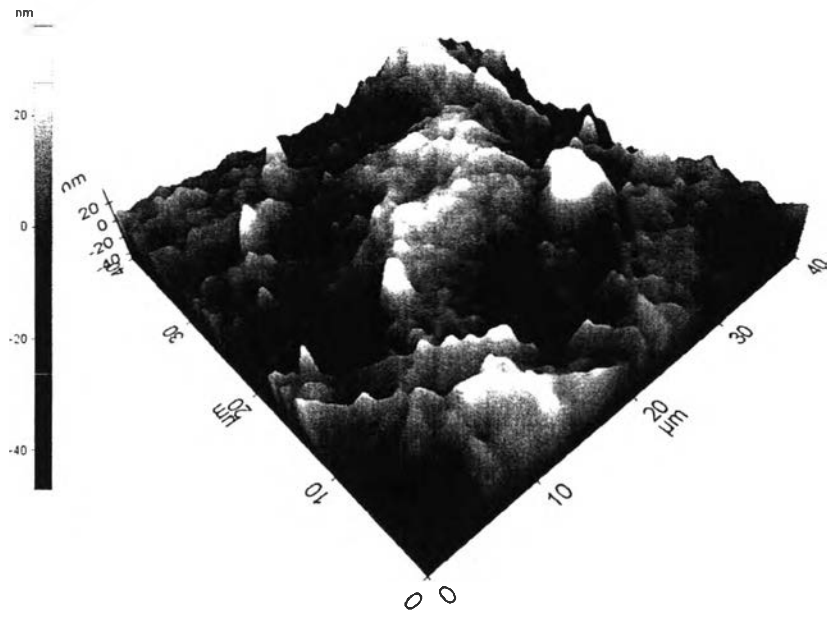


**Figure 4.18** Typical topography in 3D-profiles of the surfaces of PETG cards before exposure.

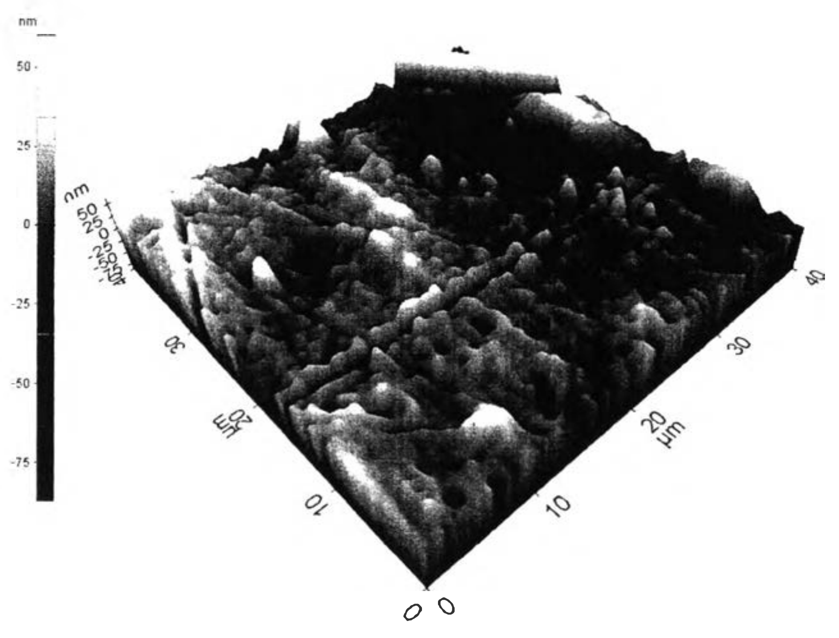


**Figure 4.19** Typical topography in 3D-profiles of the surfaces of PETG after exposure in QUV accelerated weathering tester for 15 cycles.

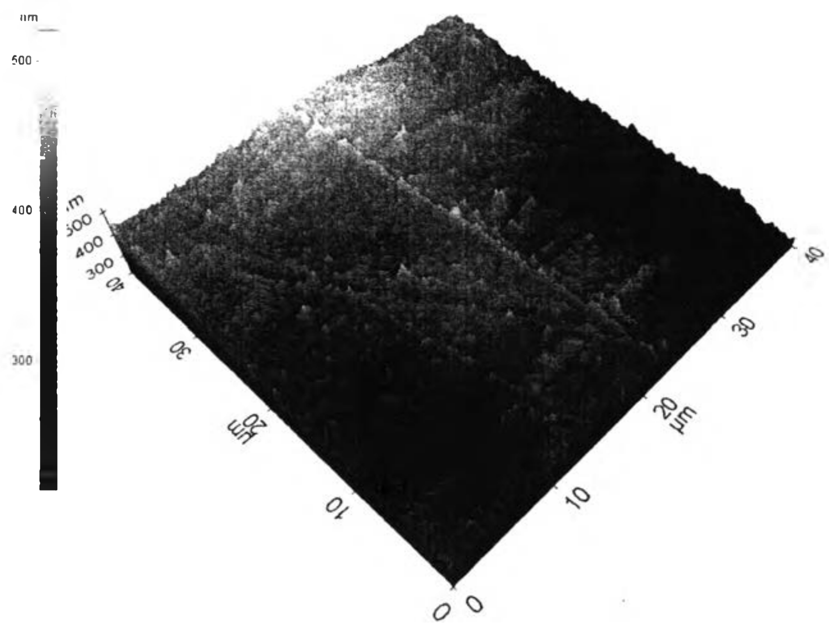


**Figure 4.20** Typical topography in 3D-profiles of the surfaces of PETG cards after outdoor exposure for 5 months.

4.4.6 Fourier transform infrared spectroscopy

The effects of exposure were demonstrated to have a considerable influence on the properties of plastic cards. Although the experiment was set in same condition and environment, the results of measurement in each material were different because of their structure.

*4.4.6.1 Polyvinyl Chloride (PVC)*

PVC cards were characterized by using FTIR to examine the functional group. The spectrum is shown in figure 4.16. PVC should not be expected to absorb at least in the near UV. Chormophoric impurities were present which might be carbonyl group due to oxidation or unsaturated structure built into polymeric during the polymerization. The FTIR spectrum shows the carbonyl absorption at 1731 $cm^{-1}$ (normally expanded in the region 2000-1500 $cm^{-1}$). Trace of monomer suggests that to some small extent the chain terminal radical was capable of depolymerising. PVC liberated hydrogen chloride that observed at 2924 $cm^{-1}$ and conjugated unsaturation, this behavior closely reminiscent of its thermal degradation (Grassie, N., *et al.*, 1985).

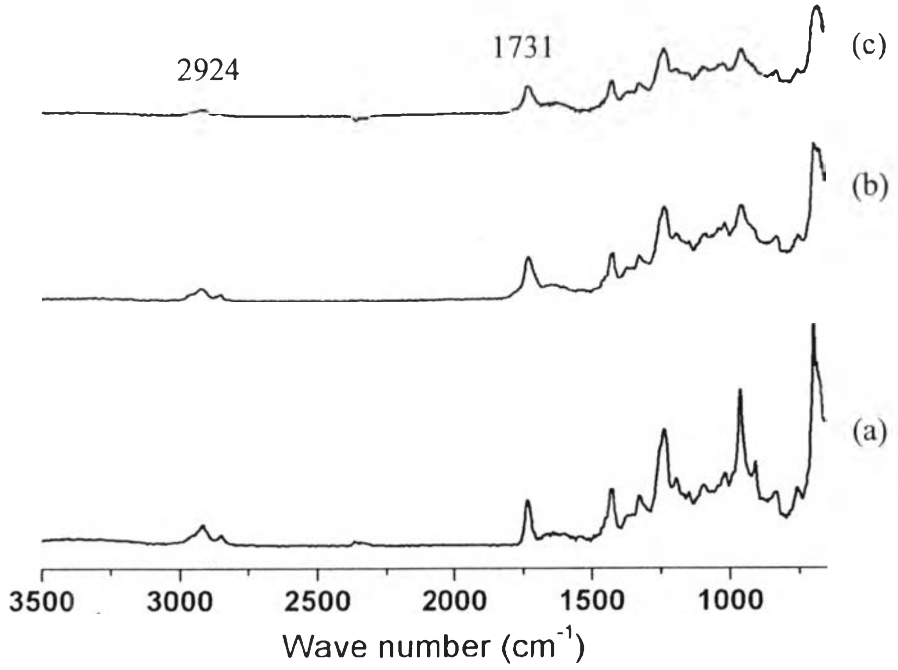


**Figure 4.21** FTIR spectrum of PVC cards, (a) FTIR spectrum before exposure (b) FTIR spectrum after exposure in QUV accelerated weathering tester for 12 cycles (c) FTIR spectrum after outdoor exposure for 6 months.

*4.4.6.2 Polyethylene Terephthalate Glycol (PETG)*

PETG cards were characterized by using FTIR to examine the functional group. The spectrum is shown in figure 4.16. In degradation of polyethylene terephthalate glycol, chain scission is also predominant. The initial break can apparently occur in the ester group. Carbon dioxide and carbon monoxide may be liberated following scission in ester group and all of the radicals formed may abstract hydrogen from elsewhere in the system (Grassie, N., *et al.*, 1985). The FTIR spectrum shows the ester group stretching band of C=O at 1711 $cm^{-1}$ and C-O at 1239 and 1093 $cm^{-1}$.This chain scission process is indicated by the reason that vinyl group at 2921 $cm^{-1}$ was formed in degradation of polyethylene terephthalate glycol (Sinnamon, B.F., *et al.*, 1999)

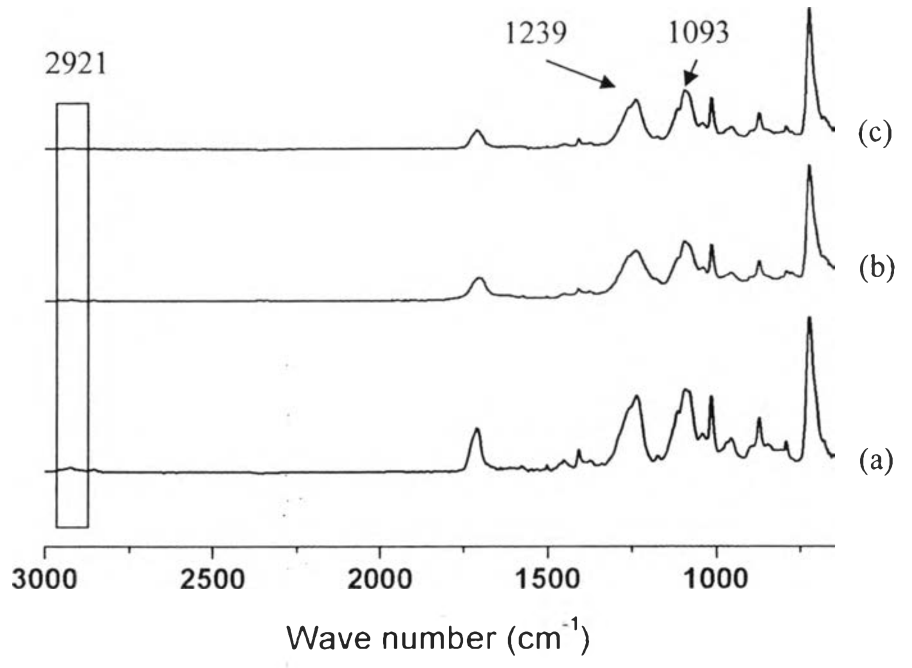


**Figure 4.22** FTIR spectrum of PETG cards, (a) FTIR spectrum before exposure (b) FTIR spectrum after exposure in QUV accelerated weathering tester for 12 cycles (c) FTIR spectrum after outdoor exposure for 6 months.

*4.4.6.3 Polycarbonate (PC)*

PC cards were characterized by using FTIR to examine the functional group. The spectrum is shown in figure 4.16. PC is relatively stable to photodegradation due to energy sink function of the aromatic rings. Aromatic hydrocarbons show absorptions in the regions 1599 cm$^{-1}$ and 1503 cm$^{-1}$ due to carbon-carbon stretching vibrations in the aromatic ring. The pattern of weak bands in the region 1767 cm$^{-1}$ reflects the substitution pattern on the ring. The pattern of the out of plane C–H bending bands in the region 887, 828, 814, 766 and 707 cm$^{-1}$ are also characteristic of the aromatic substitution pattern. Random chain scission occurs at a very slow rate with liberation of carbondioxide. The radicals formed in this sequence can undergo a series of isomerization and recombination process so that new structures become incorporated into the polymer molecules (Grassie, N., *et al.*, 1985).

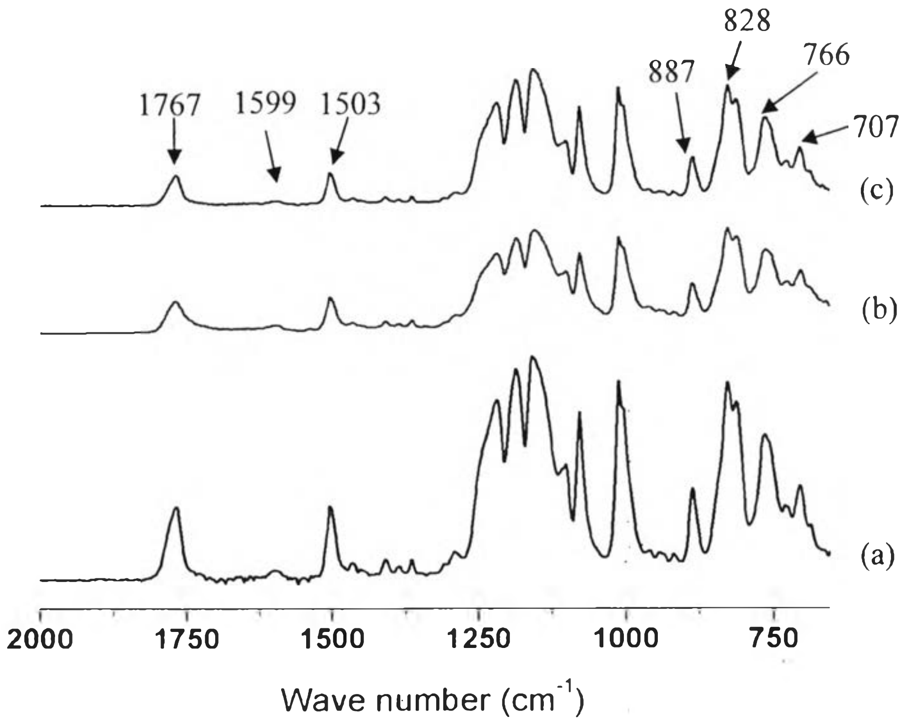


**Figure 4.23** FTIR spectrum of PC cards, (a) FTIR spectrum before exposure (b) FTIR spectrum after exposure in QUV accelerated weathering tester for 12 cycles (c) FTIR spectrum after outdoor exposure for 6 months.

## 4.5 Conclusions

PVC, PC and PETG cards were observed the degradation by moisture, light and temperature. Outdoor exposure was designed and samples were collected every month. Comparing to those on outdoor exposure, the accelerated weathering test or QUV was programmed the cycle test to deteriorate plastic cards. The gloss total color different ($\Delta E$) mechanical properties and thermal property were measured for two conditions. The accelerated weathering tester helped to determine the periods of time when plastic cards were degraded. Plastic cards were sallow and brittle when exposed to the UV for long periods of time because they were degraded by photolysis. The samples became slightly darker over time and migrated towards the yellow and green sides of the color spectrum. During the exposure process, a reduction in gloss was observed. All materials had clinically acceptable color change over time. PC exhibited the best mechanical properties. PETG exhibited the best photostability. PVC was lowest in gloss at 60° value and highest in total color different implying the least photo resistant. The FTIR spectrum show the absorption peaks of degradation in plastic cards. When exposed PC, PVC and PETG cards in Outdoor and QUV accelerated weathering tester, the FTIR spectrum peak were broad. Moreover, FTIR spectrums before exposure have the absorption peaks of degradation because of thermal degradation in manufacturing and photo degradation when testing. Three-dimensional profiles of the outdoor exposure sample surfaces were more roughness than the sample after exposure in QUV accelerated weathering tester.

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