

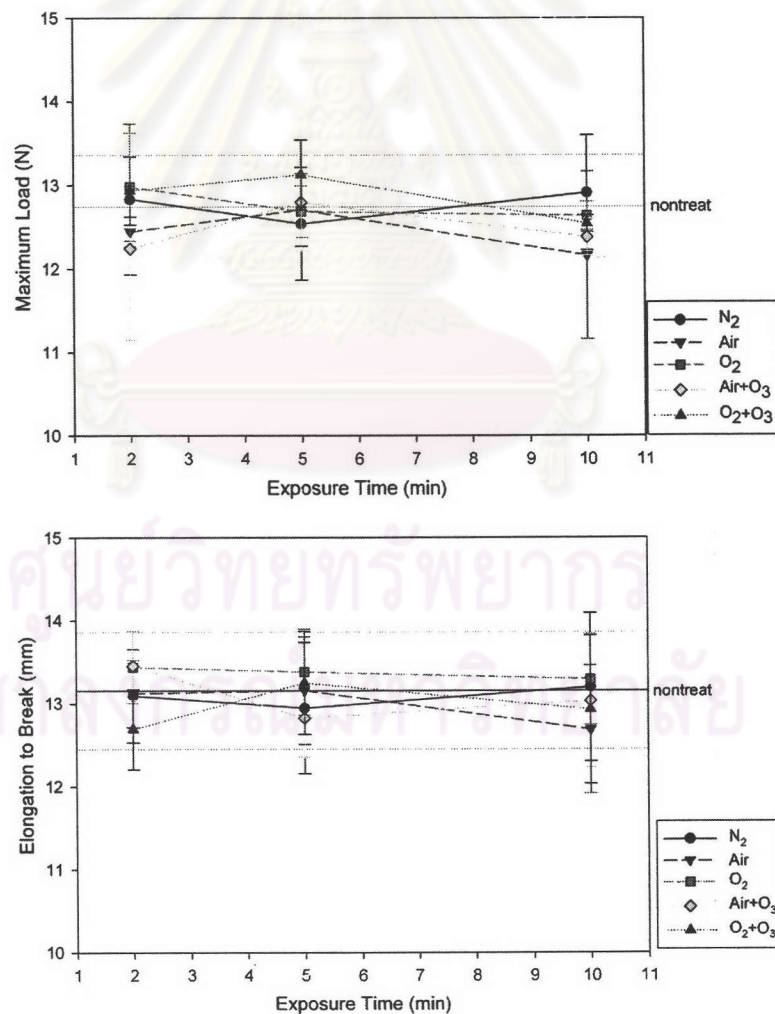
# Chapter 4

## Results and Discussion

### 4.1 Effects of Surface Treatment on Properties of PET Fiber

#### 4.1.1 Tensile Properties

In the case of textile materials, it is difficult to measure the cross-sectional area. Consequently, in this study, the behavior of PET yarns under an applied load was expressed by the load-elongation curves (Appendix A1). Figure 4.1 shows effects of gas species and exposure time of the UVO treatment on the tensile properties, maximum load and strain at break, of the yarn samples. It was evident that the treatment leads no significant changes to the tensile properties.



**Figure 4.1** Effects of gas species and exposure time of the UVO treatment on the tensile properties, maximum load (top) and elongation at break (bottom), of the yarn samples.

Both the gas species and the exposure time have no effect on the tensile properties of the yarn samples. The maximum load and the elongation of nontreated and treated PET yarns of longer exposure time, 10 minutes, remain insignificant changes compared to those at 2 minutes of exposure time. The maximum loads of all samples are within the range of 12 – 13 N where as the elongations at break of every sample are about 12.5 – 14 mm.

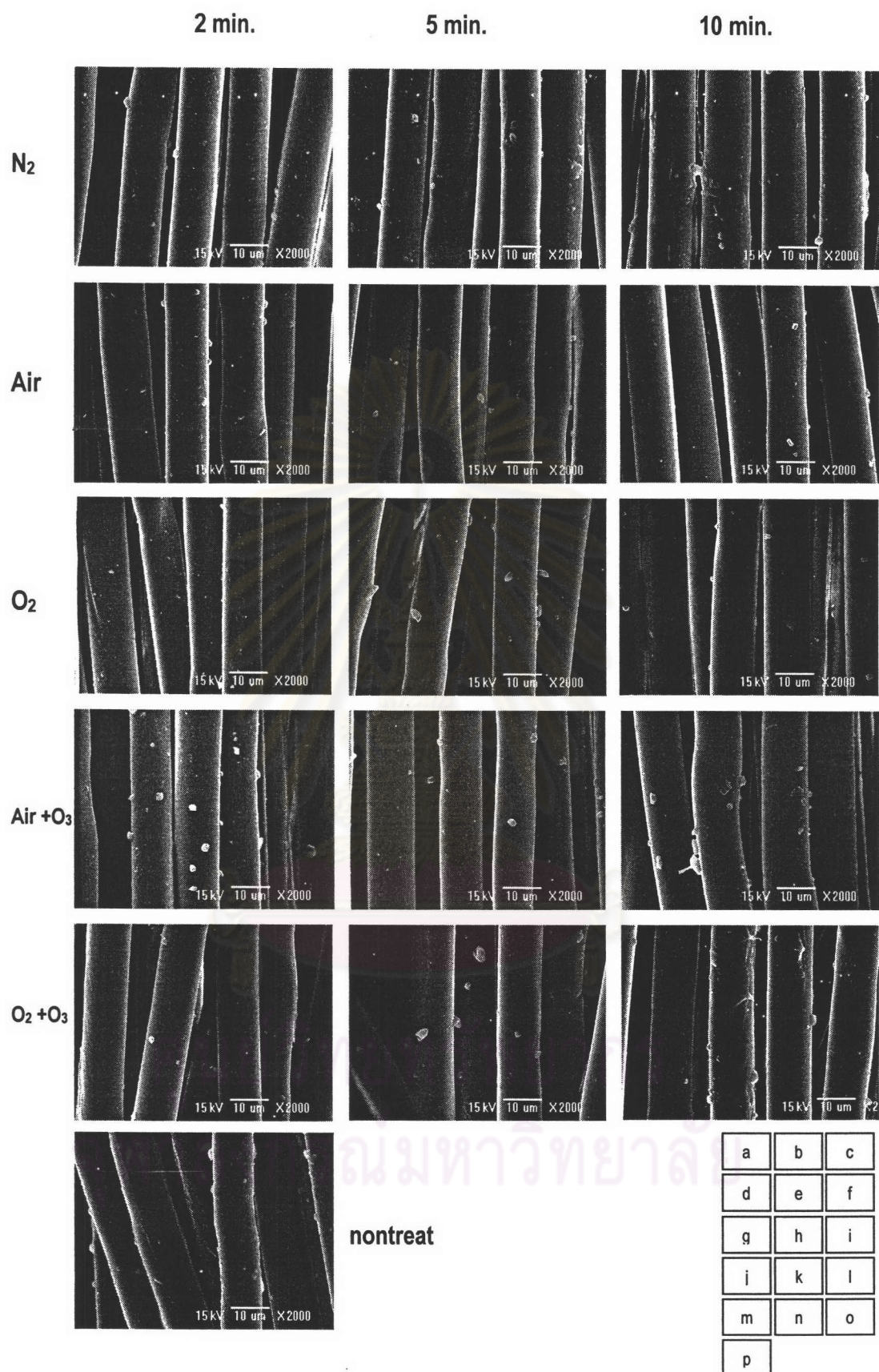
In addition, from Figure 4.1, it is indicated that the UVO treatment did not cause any adverse effects on the bulk tensile properties of PET-yarns. This result is contrasted with the results as shown in earlier investigation that the tenacity and elongation at break of jute fiber were decreased by the corona and UV/air surface treatments [52]. Hence, in our case, these results suggest that any effects that might be cause in tensile properties of PET-yarn/epoxy composites should be affected by altering the interface's properties between PET and epoxy, not by the yarns itself.

#### *4.1.2 Surface Morphology*

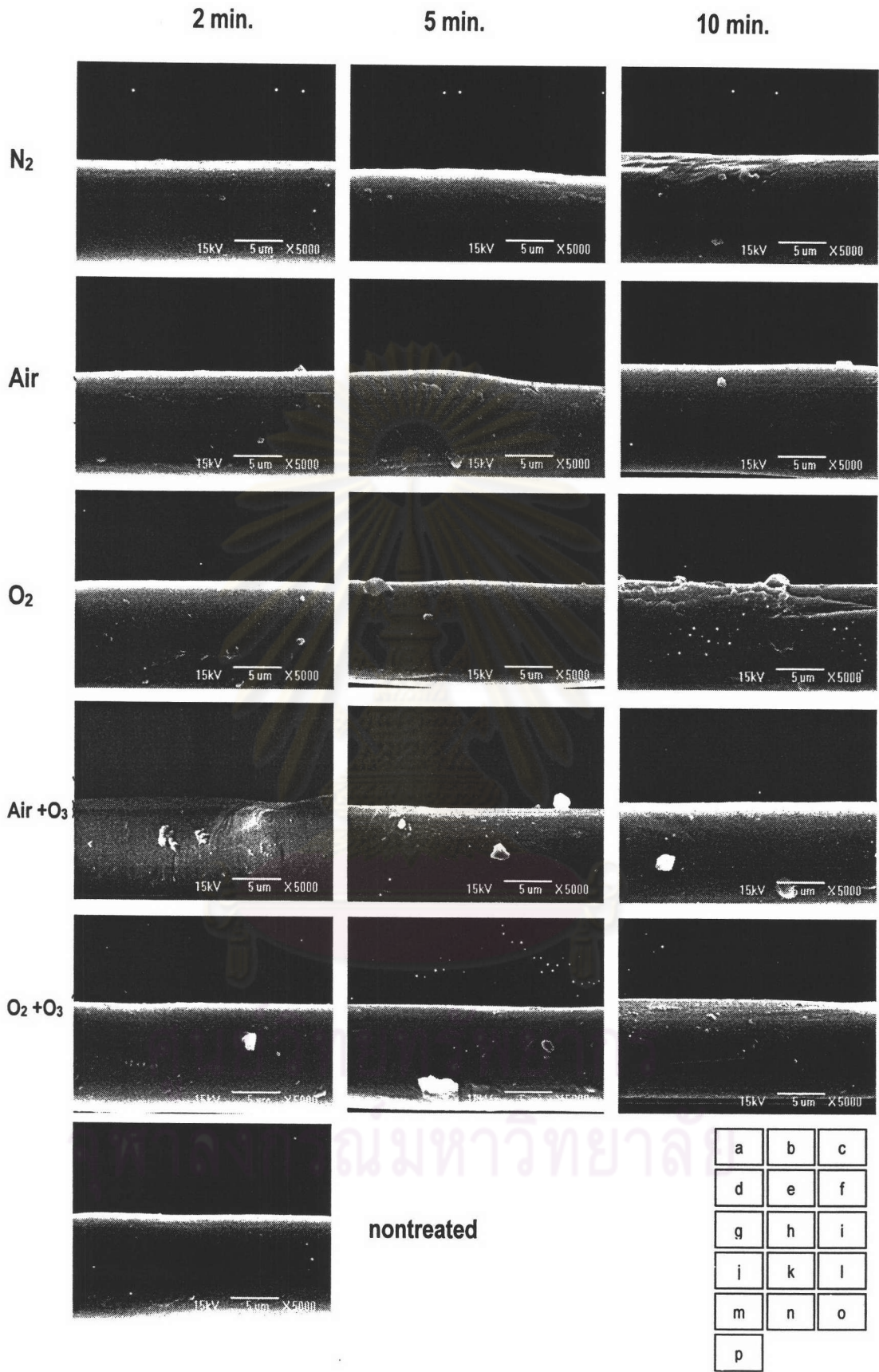
Surface morphology plays important roles to fiber-matrix interactions, especially roughness, which can be caused in an increase of mechanical bonding and wettability of fiber. In this study, the surface morphologies of PET-yarns both before and after UVO treatments with various regimes were examined by scanning electron microscopy. Figure 4.2 and Figure 4.3 summarize the SEM micrographs of PET yarn samples at x2000 and x5000 magnification, respectively. However, due to the limitations of the technique, only two dimensional and micro-scale of surface morphology can be observed.

Obviously, as shown in both figures, the PET yarn had a smooth surface with some small artifacts. The SEM micrographs revealed no significant changes in surface roughness of treated fiber in micro-scale. Similar to the tensile properties, both gas species and exposure time did not affect the surface morphology of the PET yarn, at least not with in this micro-scale technique. The interaction between fiber surface molecules and UV/gas species might have increased the total surface area and nanoscale topography, as those previously reported for PET film systems [4, 49, 51]. However, surface topographical having dimensions less than 100 nm should not significantly affect wettability [49].





**Figure 4.2** SEM micrographs of PET-fiber before an after UVO treatment with different regimes, the scanning area was 66  $\mu\text{m}$  X 49.5  $\mu\text{m}$ .



**Figure 4.3** SEM micrographs of PET-fiber before and after UVO treatment with different regimes, the scanning area was 26.4 μm X 19.8 μm.



#### 4.1.3 Oxygen content of the PET surface

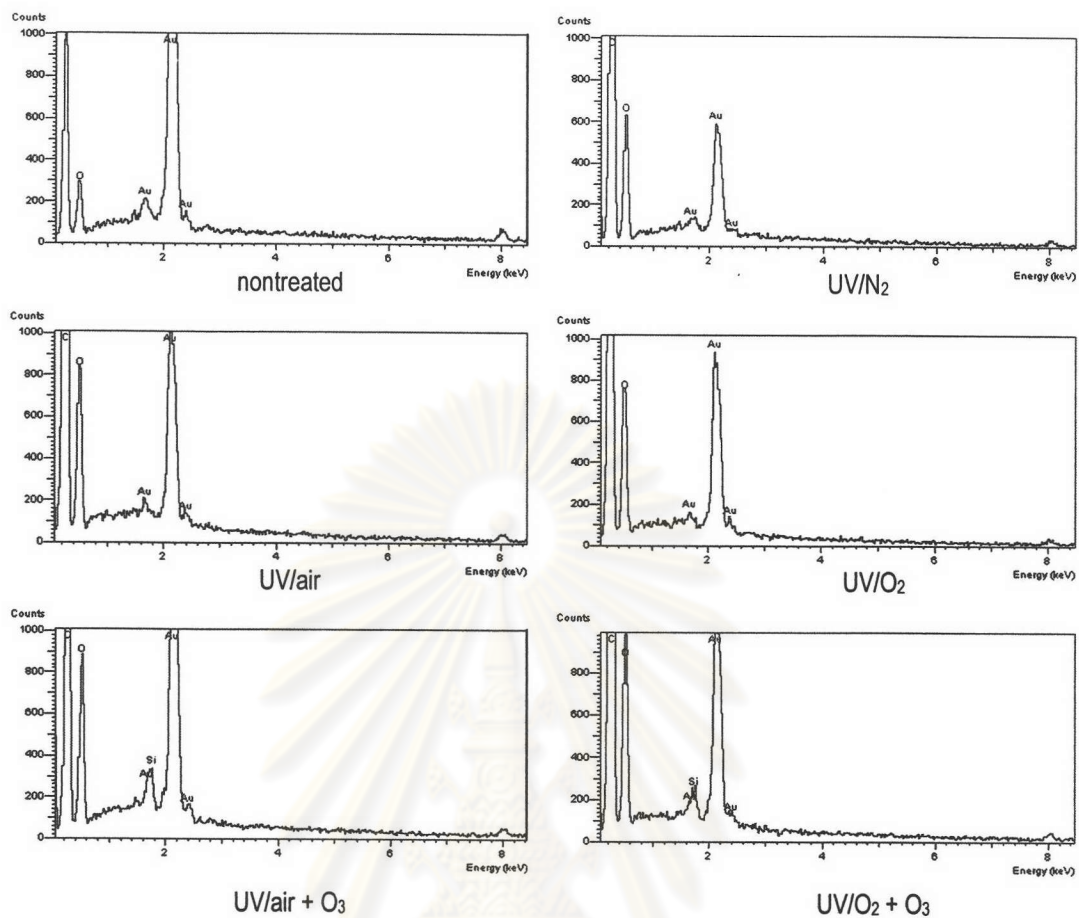
According to previous FTIR analysis by M. Strobel et al. [49], the modification of PET films by UVO technique was in the order of 1  $\mu\text{m}$  deep. Therefore, it is worth to preliminarily analyze both before and after treated PET yarn by using SEM/EDX technique, which can probe depths from 0.2 to 8  $\mu\text{m}$ . The probe depth of the SEM/EDX technique depends on the energy of the electron beam used and the average atomic number of the sample [32]. In this study, EDX analysis with a 15 kV accelerating voltage of the electron beam was used to determine the effects of UVO treatment on the oxygen content of PET yarn surfaces.

Because PET is an oxygen-containing polymer, the oxygen uptake from the surface treatment was expressed as " $\Delta\%O$ ", the difference between the oxygen content of treated sample and the oxygen content of nontreated PET yarn. The  $\Delta\%O$  values were simply the increase in the amount of oxygen as detected by SEM/EDX. Oxygen contents were calculated using areas under the atomic oxygen characteristic peak. Table 4.1 summarizes the oxygen contents and  $\Delta\%O$  values of PET yarn surfaces before and after 10 minutes treatment with different gas species. Figure 4.4 shows examples of EDX spectra of PET yarn surfaces before and after 10 minutes treatment with different gas species.

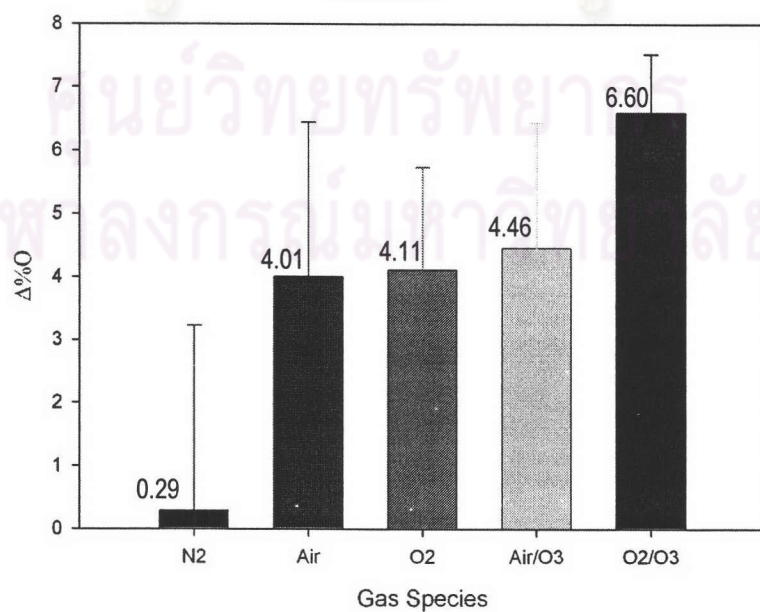
Figure 4.5 shows the comparative results of  $\Delta\%O$  on the PET yarn surfaces after 10 minutes treated with various gas species. The results clearly indicated that treating of PET yarn with oxygen-containing gas species, i.e. air,  $O_2$ , air +  $O_3$ , and  $O_2$  +  $O_3$ , increased oxygen contents of the PET fiber surfaces.

**Table 4.1** Oxygen contents and  $\Delta\%O$  values of PET yarn surfaces before and after 10 minutes treatment with different gas species.

Treatment Regimes	Oxygen Content (%)	$\Delta\%O$
Nontreated	29.91	-
UV/ $N_2$	30.20	0.29
UV/air	33.92	4.01
UV/ $O_2$	34.02	4.11
UV/air + $O_3$	34.37	4.46
UV/ $O_2$ + $O_3$	36.51	6.60



**Figure 4.4** EDX spectra of PET yarn surfaces before and after 10 minutes treatment with different gas species



**Figure 4.5** Effect of gas species on the  $\Delta\%O$  of treated PET yarn



Polymers such as PET absorb light because of the presence of chromophoric functionalities in the polymer backbone (c.f. 2.10.2), the cut-off wavelength of 310 nm. The changes that can be occurred in PET upon absorption of UV light include the formation of carboxylic acid end groups, terminal vinyl groups, phenols, and the evolution of CO and CO<sub>2</sub> [44]. These changes take place by direct photocleavage via Norrish type I and Norrish type II scission processes involving the ester group. Support for the formation of these groups was provided in part by works of Peeling et al. [38], M.J. Walzak [44], and R.H. Bradley [4]. The reactions that take place at the PET surface are known to be complex and give rise to a variety of functional groups. However, the functional groups mentioned above are simply the oxygen insertion to the PET surface. By insertion of oxygen through reactions, the wettability of PET was increased significantly [44, 45]. In this work, we were not interested in investigation of the functionalities occurred on treated surfaces, but the increasing of the oxygen content on the treated surfaces. We assumed that any increasing of oxygen content on the PET surface might increase the wettability and bonding of PET fiber surface to epoxy matrix.

From EDX results, nontreated PET yarn surface contained 29.91 % of oxygen atom. Using the five different regimes of UV/N<sub>2</sub>, UV/air, UV/O<sub>2</sub>, UV/air + O<sub>3</sub>, and UV/O<sub>2</sub> + O<sub>3</sub> allowed us to evaluate the relative importance of the presence of oxygen, oxygen concentration, presence of ozone, and ozone concentration in modifying the surface of PET yarn. With the UV/N<sub>2</sub> regime the  $\Delta\%O$  values was lowest compared with other regimes due to the absent of reactive gas species. Slightly increase of oxygen content with this regime, 0.29 %, or increased to 30.20 %, revealed small effects of UV radiation on the PET yarn surface.

In the case of treatments with oxidative gas species, i.e. UV/air, UV/O<sub>2</sub>, UV/air + O<sub>3</sub>, and UV/O<sub>2</sub> + O<sub>3</sub>, the oxygen contents of PET surfaces were much more increased compared to UV/N<sub>2</sub> treatment, as expected. The UV/air treatment, low oxygen concentration of condition, increased the oxygen content of PET surface to 33.92 % ( $\Delta\%O = 4.01$  %). This amount of oxygen content was similar to the results given by UV/O<sub>2</sub> treatment which increased the oxygen content of PET surface to 34.02 % ( $\Delta\%O = 4.11$  %). It was evident that the presence of oxygen gas caused a considerable change of oxygen uptake to the PET surface. In contrast, oxygen concentration of gas species did not appear to affect the oxygen uptake. These results might be due to the limited reactivity of oxygen gas.

Effect of the presence of ozone on  $\Delta\%O$  values can be clearly seen from comparing UV/air with UV/air + O<sub>3</sub> and UV/O<sub>2</sub> with UV/O<sub>2</sub> + O<sub>3</sub>. The UV/air + O<sub>3</sub> represent a low oxygen and ozone concentration condition, which increased oxygen content on PET surface to 34.37 % ( $\Delta\%O = 4.46$  %). In this case, oxygen uptake was 0.45 % higher than UV/air treatment. This slightly increase of oxygen content might be caused by the presence of ozone. However, the ozone concentration of UV/air + O<sub>3</sub> condition ( $2.13 \times 10^{16}$  molecules per cm<sup>3</sup>) might be insufficient to cause a considerable change to the surface. This was contrasted with the comparison between UV/O<sub>2</sub> and UV/O<sub>2</sub> + O<sub>3</sub>. The high oxygen and ozone concentration condition, UV/O<sub>2</sub> + O<sub>3</sub>, yielded the highest value of oxygen content, 36.51 % ( $\Delta\%O = 4.46$  %), which was 2.49 % higher than UV/O<sub>2</sub> treatment. This might be due to the much grater value ozone concentration for UV/O<sub>2</sub> + O<sub>3</sub> condition, about  $6.12 \times 10^{16}$  molecules per cm<sup>3</sup>, which was almost three time higher than UV/air + O<sub>3</sub> condition. This ozone concentration might sufficient to cause a considerable change to PET surface, leading us to conclude that the presence and sufficient concentration of ozone increase amount of oxygen uptake on the PET yarn.



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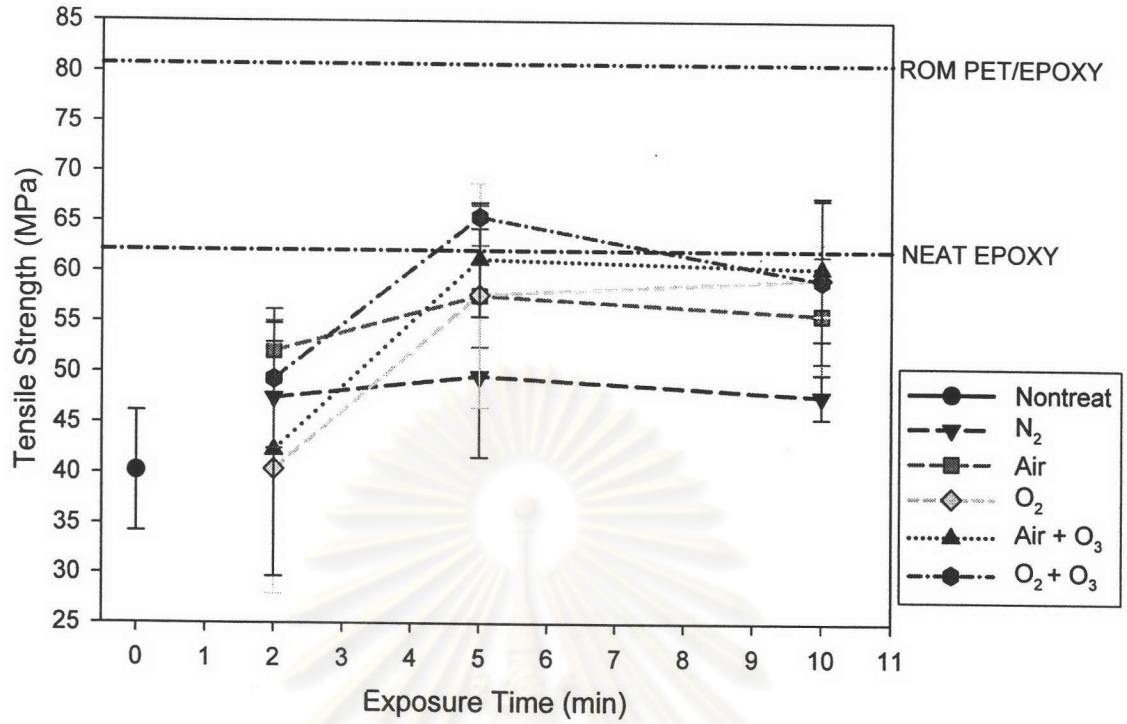
## 4.2 Effects of Surface Treatment on Tensile Properties of PET/Epoxy Composite

Tensile specimens were fabricated by method described in section 3.3.1.6. Effects of UVO surface treatments of PET yarns on three important tensile parameters, i.e. the tensile strength, elongation to brake, and toughness of PET/epoxy composite were investigated and shown in Figure 4.6 – 4.8, respectively.

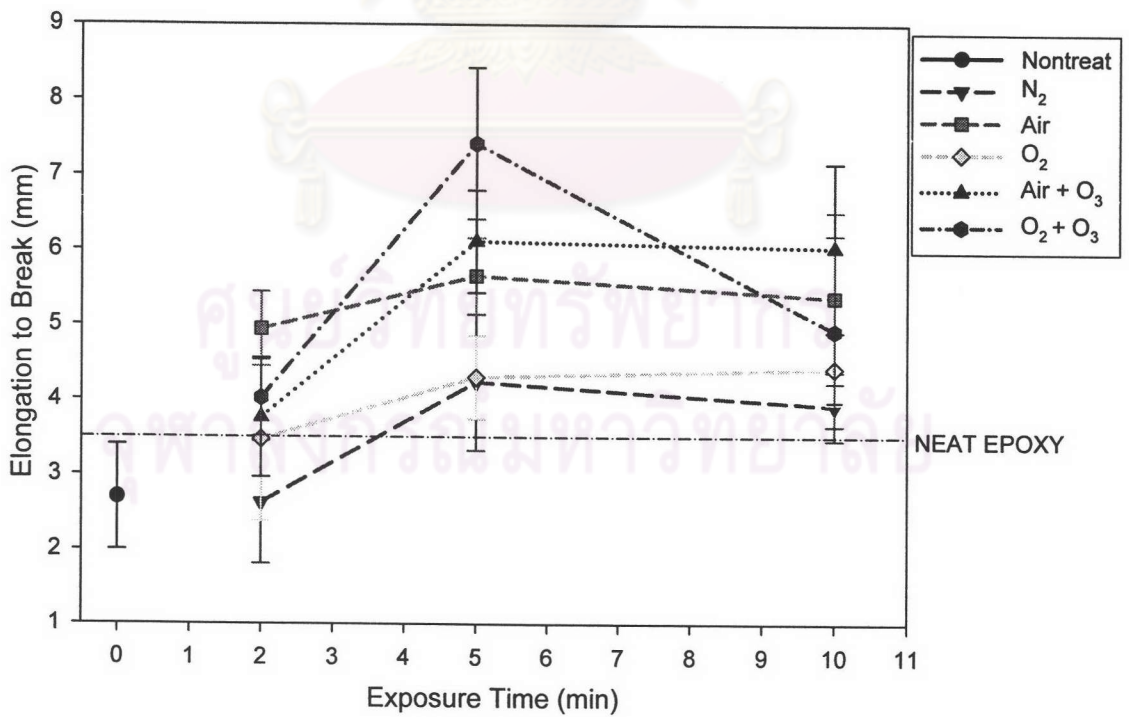
For tensile strength, in order to assess the effectiveness of the fibers at contributing to the effective composite tensile strength, the results were compared relatively to the ideal case, in which the tensile strength of the composite was predicted by 'Rule of Mixture' (ROM) or isostrain condition as mentioned in section 2.6.1. The predicted value represents a behavior of composite that possesses perfect, rigid-elastic, interface between PET fiber and epoxy matrix. However, ROM was not employed to predict other two parameters, elongation to brake and toughness, because these two properties involve with complex failure mechanism. Neat properties of epoxy resin were also used in order to evaluate and compare roles of presence of fibers before and after treatment which can alter the mechanical properties of the materials.

To analyze these tensile properties, the fractography of the composites should be helpful to understand modes of failure mechanism under an applied load with constant strain rate. Interface studies of nontreated and surface modified PET fiber/epoxy composites were carried out to investigate failure mechanism such as fiber splitting, fiber pullout, debonding, matrix cracking and fiber - matrix interaction by scanning electron microscopy. Figure 4.9 and Figure 4.10 show the fractography of the composites before and after treatment with different regimes, the magnifications were x500 and x1000, respectively.

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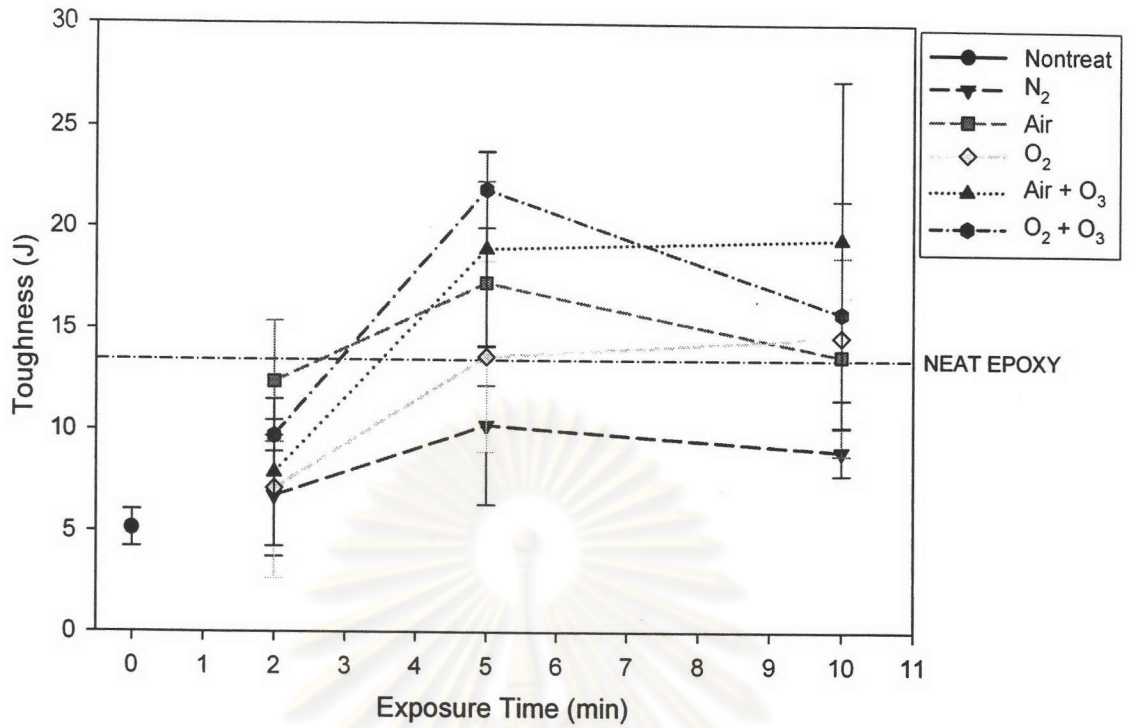


**Figure 4.6** Effects of UVO surface treatment with various gas species on the tensile strength of the composites



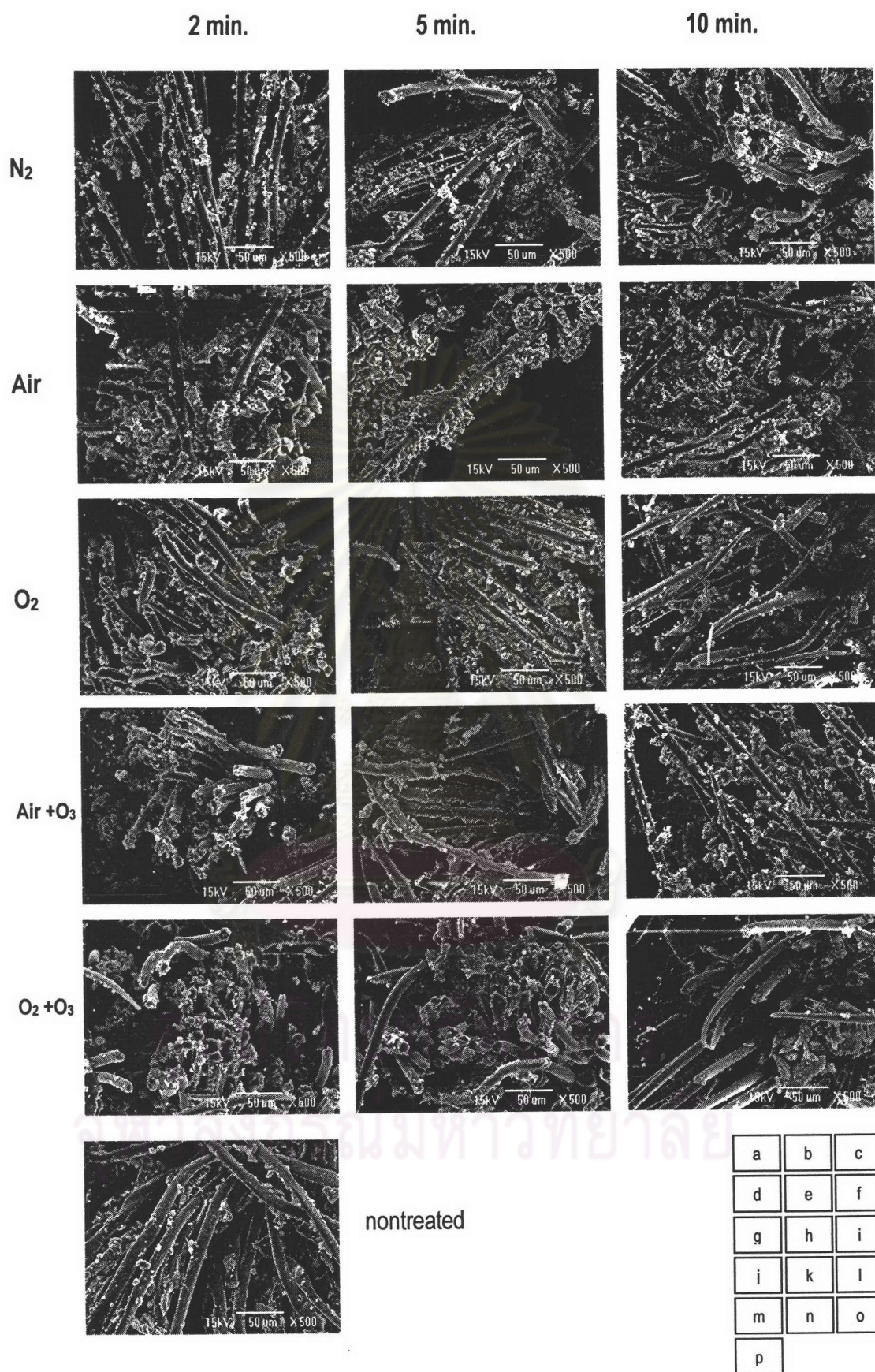
**Figure 4.7** Effects of UVO surface treatment with various gas species on the elongation to break of the composites





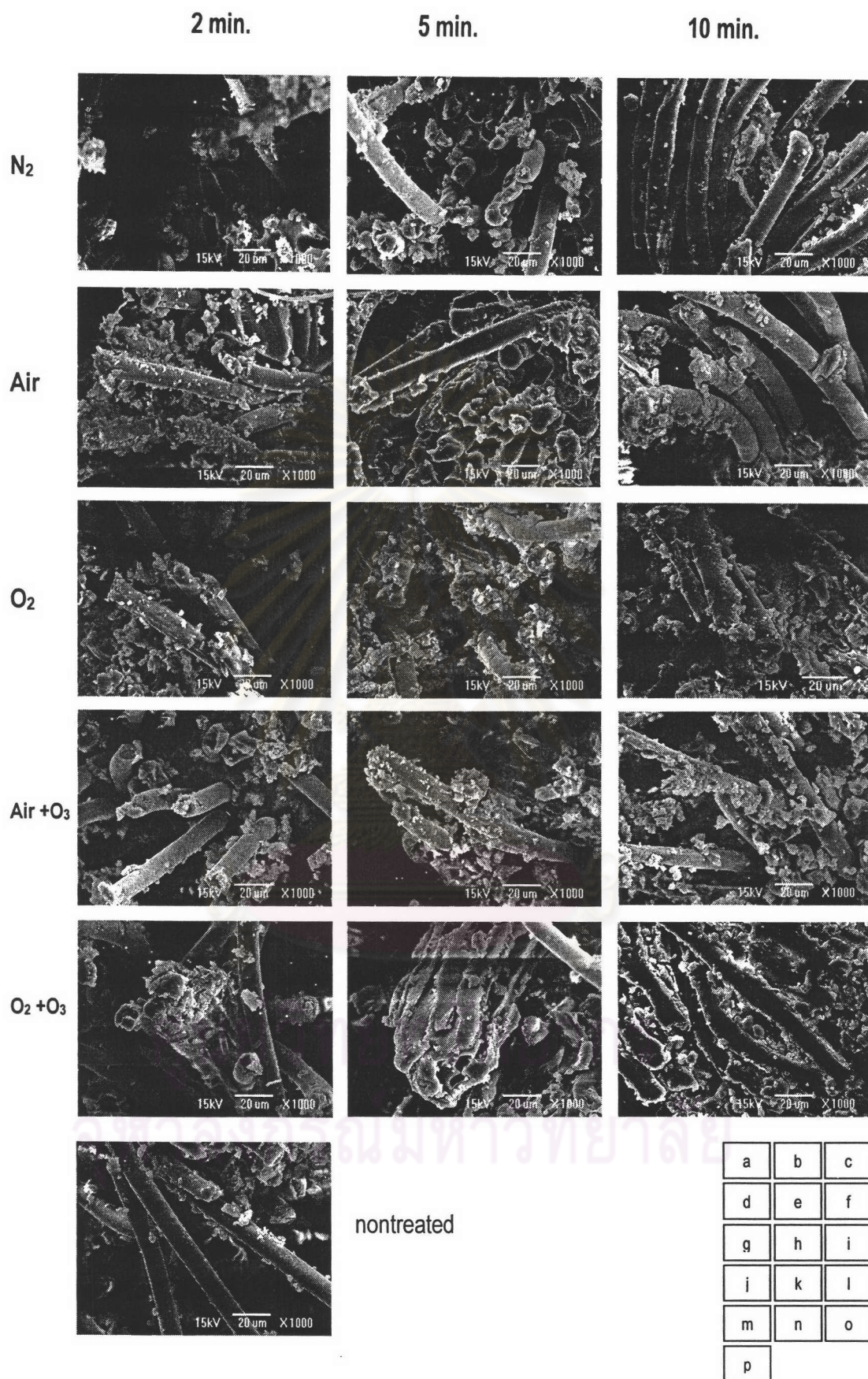
**Figure 4.8** Effects of UVO surface treatment with various gas species on the toughness of the composites

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**Figure 4.9** Scanning Electron Microscope fractographs of tensile specimen, x500 magnification, scanning area = 264 μm X 196 μm.





**Figure 4.10** Scanning Electron Microscope fractographs of tensile specimen, x1000 magnification, scanning area = 132  $\mu\text{m}$  X 98  $\mu\text{m}$ .



From Figure 4.6 - 4.8, all three tensile properties of the composites, i.e. tensile strength, elongation to break, and toughness, were decreased when nontreated PET yarn was incorporated into the epoxy matrix. PET fiber seemed to behave like a defect, which reduces mechanical properties of resulted composite. Defection of the composite via nontreated PET fiber can be seen in Figure 4.9(p) and 4.10(p). It was evident that clean and smooth surface of fibers and many holes left after the fibers were pulled out from the matrix, indicated that the failure occurred at weak fiber/matrix interfaces. Length of the fiber pulled out from the matrix part was very long. From these results, it might be possible to conclude that the failure mechanisms of the nontreated PET/epoxy composite was mainly by fiber pull-out resulted from weak fiber/matrix adhesion and/or compatibility.

In comparison to the neat epoxy with an average tensile strength of 62 MPa, the nontreated fiber composite showed an average tensile strength of 40 MPa. This result which indicated that despite to an increase in the tensile strength as predicted by ROM (Figure 4.6), a significant decrease in mechanical strength occurred. Similarly, elongation to break and toughness were reduced from 3.5 mm and 13.5 J to 2.7 mm and 5.1 J, respectively. Hence, the PET fiber showed adversely effects on the tensile properties when it was incorporated into the neat matrix.

For UV/N<sub>2</sub> treatment regime, a slight increase in tensile strength, elongation to break, as well as toughness was observed. This result is in good agreement with the  $\Delta\%O$  values of UV/N<sub>2</sub> treatment as discussed in section 4.1.3. In principle, for this regime, we assumed that only UV light affects the surface properties of PET fiber, the properties of composites should not change since nitrogen is an inert gas for a reaction. However, some adhesion between PET fiber and epoxy matrix can be observed from Figure 4.9(a) - (c). The UV/N<sub>2</sub> treated PET fiber surfaces had greater amount of epoxy adhered to the pulled fiber more than those observed in nontreated fiber composite. This might be caused by existing of some reactive species contaminated inside the reactor during treatments, e.g. moisture and oxygen. Nevertheless, the UV/N<sub>2</sub> treated fiber still behaved as a defect rather than as a reinforcement judging from the lower in tensile strength and toughness values of the composites compared to those of epoxy resin matrix.



From the SEM micrographs of UV/N<sub>2</sub> treated fiber composites, we can notice the delamination of the composites (Figure 4.9(b) and 4.10(b)), which represents debonding mechanism located and propagated along the fiber/matrix interface. This mechanism leads to further weakening in the composite. Considering the effects of exposure time, there was also no significant role to the tensile strength of the composites upon increasing exposure time of UV/N<sub>2</sub> treatment. However, an increase in exposure time has improved both the elongation to break and toughness of the composites.

At initial stage of surface treatment, 2 minutes, UV/air regime seemed to be the most superior condition for increasing tensile properties. When compared the UV/air regime with other UV/oxygen-contained regime, it was indicated that at the initial stage the concentration of oxygen and the presence of ozone were not predominate parameter affecting rate of surface reactions. The fractographs of 2 minutes UV/air and UV/O<sub>2</sub> treated composites (Figure 4.9(d), 4.9(g), 4.10(d), and 4.10(g)) revealed failure mechanism that was similar to those nontreated and UV/N<sub>2</sub> regimes, however, higher amount of epoxy matrix adhered to the pulled out fiber was observed in the case of UV/air and UV/O<sub>2</sub> treated. For ozone-contained regimes, UV/air + O<sub>3</sub> and UV/O<sub>2</sub> + O<sub>3</sub>, shorter length of pulled out PET fiber from the epoxy matrix can be seen from Figure 4.9(j) and 4.9(m), which revealed a reduction in fiber pulled out. However, delamination was also observed in the case of UV/air + O<sub>3</sub>, as supported by their poor mechanical properties. These results may suggest that short treatment time (2 minutes) was not enough to improve mechanical properties of the composites.

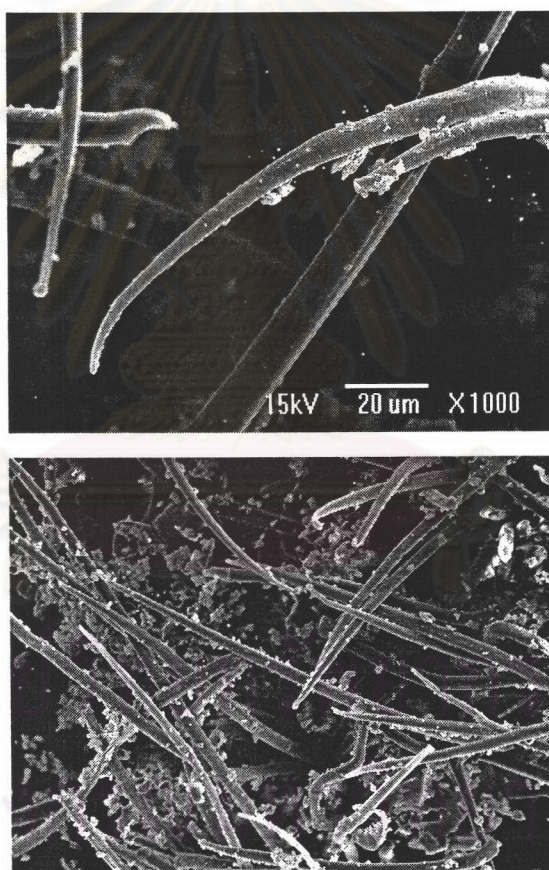
Composites exhibited differently when PET fiber was treated at intermediate exposure time (5 minutes). It was clearly seen from the fractographs a considerable improvement of the adhesion at the interface was observed and there was hardly any clean surface on the pullout fibers. Almost every parts of the fiber surface were covered with epoxy matrix. Particularly in the case of UV/air regime, the pulled out fibers were covered with layers of epoxy matrix, which indicated that strong bonding was existed between PET fiber and epoxy matrix. In this case, 5 minutes of UV/air treatment, cracks were developed in the matrix, due to stronger interaction between fiber and matrix, instead of the interface. Unlike at 2 minutes treatment, despite the grater amount of epoxy matrix or a considerable increase in strong bonding between the two phases, the tensile properties of UV/air treatment composites exhibited slightly increase compared with other regimes.

At this treatment time, the UV/O<sub>2</sub> + O<sub>3</sub> treated fiber composite exhibited highest tensile properties. This condition was considered to be an adequate treatment for PET fiber/epoxy matrix composite. The tensile strength, elongation to break, and toughness of the composites were increased 5.5 %, 112%, and 62.5%, respectively, compared to neat epoxy resin. Although the incorporation of the 5 minutes UV/O<sub>2</sub> + O<sub>3</sub> treated PET fiber seemed to help toughening the matrix rather than reinforcing as expected by ROM, the interaction between phases was still improved by the treatment. Figure 4.10(n) shows a bundle of fractured fibers with high amount of epoxy resin adhered or coated in the boundary of fibers indicating strong interface. Cracks were propagated perpendicular to fiber alignment direction indicating that fibers were trapped in the matrix rather than those other regimes, which leads to an improvement the in tensile properties of the composites.

However, tensile strength of the composites seemed to be decreased upon increasing treatment time to 10 minutes, excepted for the UV/O<sub>2</sub> treatment. At this regime, their tensile properties were slightly increased. In the case of 10 minutes UV/O<sub>2</sub> + O<sub>3</sub> treatment composite, considerable decreases of all three tensile properties, i.e. tensile strength, elongation to brake, and toughness, were observed. From Figure 4.9(i), 4.9(l), and 4.9(o), the fractographs of 10 minutes treatment of UV/O<sub>2</sub>, UV/air +O<sub>3</sub>, and UV/O<sub>2</sub> + O<sub>3</sub>, we can observe fiber fractured with ductile ends, which emphasized strong interface between fiber and matrix. Other SEM fractographs that can be clearly presented morphology of the broken ends of the PET are shown in Figure 4.11. This failure mode was not observed in the shorter treatment time. In principle, the ductile ends of the fiber normally affect and correspond to increase in tensile properties of the composite, especially elongation to break and toughness, since it is an energy-absorption mechanism. However, the results were contrasted to what we expect for, since only increasing of tensile properties of UV/O<sub>2</sub> treatment composite upon increasing treatment time to 10 minutes can be observed. This was contrasted with UV/air +O<sub>3</sub> treatment regimes decreased their tensile strength and elongation to break, as well as UV/O<sub>2</sub> + O<sub>3</sub> which all three tensile properties were decreased.



The reduction of tensile properties might be explained by the formation of low molecular weight oxidized materials (LMWOM) on fiber surface. It was well documented in the literatures (for examples, the works of M.J. Walzak [44] and Peeling [38]) that treatment of PET surface using UV/air and UV/air + O<sub>3</sub> resulted in considerable LMWOM on the surface, particularly when treatment time was prolonged. LMWOM was loosely bond to the surface since it can be readily removed by water washing. In our cases, LMWOM might be existed on the treated PET surface, particularly when the surface was treated with 10 minutes UV/O<sub>2</sub> + O<sub>3</sub> treatment which the EDX result indicated large amount of oxygen uptake to the PET surface. The presence of LMWOM might be interfered the load-transfer mechanism through the interface between PET fiber and the matrix caused adversely effect to improve mechanical properties to the composites.



**Figure 4.11** SEM fractography of PET/Epoxy matrix composite specimen: UV/O<sub>2</sub> + O<sub>3</sub> treated for 10 minutes, scanning area = 132  $\mu\text{m}$  x 98  $\mu\text{m}$  (top), UV/O<sub>2</sub> treated for 10 minutes, scanning area = 660  $\mu\text{m}$  x 490  $\mu\text{m}$  (bottom).