

# Poly(phenyl acrylate) and Poly(*p*-methylphenyl acrylate) as photo-stabilizers II. Protection of PET against photo-oxidation

Cheng-Tzu Lee, Chih-Hung Wu, Mu-Shih Lin\*

*Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050*

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## Abstract

Poly(phenyl acrylate) (PPA) and poly(*p*-methylphenyl acrylate) (PMPA) were used as inherent photo-stabilizers for PET. PPA/PET and PMPA/PET in weight ratios of 0/100, 5/95, 10/90, 20/80 and 100/0 were blended. These blends were then cast into films and drawn into fibres and were irradiated with an accelerated weathering tester (QUV). Functional group changes in the films during irradiation were monitored with FTIR and the absorbance changes for different samples were compared with one another. Tensile strength of fibres after 42 days of irradiation were tested. Experimental results revealed that when 5% of PPA or PMPA was incorporated into PET, good stabilization of the film and fibres were observed, with PMPA exhibiting more photo-stabilization capability and better retention of tensile strength after 42 days of accelerated aging.

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*Keywords:* Photo-oxidation; Photo-stabilizer; Accelerated ageing; Functional group changes; Retention of tensile strength

## 1. Introduction

PET is a commercially available polymer and is widely used as fibre, textile, bottle, video tape, food trays and other consumer products. Outdoor use of PET is very common. Therefore, its weatherability becomes an important consideration. Photo-stabilization of PET can be achieved by various means. These include screening of ultraviolet light, deactivation of excited states, addition of radical scavengers, and so on. Use of UV absorber to retard the adverse effect of irradiation is another possibility. The UV absorber absorbs harmful UV and converts it into a harmless form. However, discoloration may, sometimes, be a drawback. The most widely used UV absorbers are low molecular weight derivatives of *o*-hydroxybenzophenones, salicylic esters, and benzotriazoles [1,2]. However, leaching might be a problem for these low molecular weight UV absorbers. Therefore, we are interested in using a polymeric type of photo-stabilizers to avoid leaching problem and, in addition, to avoid the mechanical limitations. In our previous study on the kinetics of photo-Fries rearrangement [3], both PPA and

PMPA, upon irradiation of UV ranging from 275 to 360 nm, underwent intra-molecular photo-Fries' rearrangement [4–9] with a first-order of reaction. We found that PPA produced both *o*- and *p*-hydroxybenzophenone moieties with a rate constant of  $3.59 \times 10^{-7} \text{ s}^{-1}$ , while PMPA produced only *o*-hydroxybenzophenone moiety with a rate constant of  $4.53 \times 10^{-6} \text{ s}^{-1}$  [3]. Of the *o*- and *p*-hydroxybenzophenone, only the ortho form acts as an effective UV-absorber [1–3] since PMPA produced *o*-hydroxybenzophenone more effectively and therefore was believed to be a more effective inherent photo-stabilizer than PPA. In this paper, we report our further study on their field tests of photo-stabilization of PET.

## 2. Experimental

### 2.1. Sample preparations

PPA and PMPA were synthesized as reported elsewhere [3]. PET with an intrinsic viscosity of 1.0 was obtained from Far Eastern Textile Ltd. (Taiwan). PPA/PET and PMPA/PET in weight ratios of 0/100, 5/95, 10/90, 20/80 and 100/0 were dissolved in phenol. Films were spin-coated on aluminium foil and dried in the

\* Corresponding author. Tel.: +886-35-712-121; fax: +886-35-723-764.

vacuum oven over night. The same weight ratios of PPA/PET and PMPA/PET were also blended with a Brabender mixer, and then were drawn into fibres.

## 2.2. Instruments

Glass transition temperatures ( $T_g$ 's) were detected with Seiko SSC 5200 differential scanning calorimeter (DSC). Accelerated aging tests were studied with a Q-panel Company weathering tester with eight UVB-313 fluorescent UV lamps (each lamp 40 W, wavelength ranging from 275 to 360 nm). Tensile strength of fibres were tested with an Orientec Tensilon RTA-1T with load cell of 1 kg.

Functional group changes were investigated with a Nicolet 520 FTIR spectrometer with a resolution of  $1\text{ cm}^{-1}$ . Difference spectra,  $A_t - A_0$  were obtained by subtracting the absorbance at an irradiation time  $t$  from that before UV ageing, using the aromatic ring absorbance at  $1595\text{ cm}^{-1}$  as internal standard.

## 3. Results and discussions

PET undergoes photo-degradation and photo-oxidation when it is exposed in outdoor application. The degradation mechanisms and products are extensively reported in the literature [10–12]. Degradation could result in deterioration of physical properties, such as loss

of tensile strength and impact resistance, embrittlement, surface crazing and discoloration. Photodegradation products include CO, CO<sub>2</sub>, hydrogen, methane, ethane, benzyl end groups, etc. By-products that are hydroxylated in the benzene ring and aliphatic positions and few crosslinking molecules are also found. Fig. 1 shows the IR spectrum of PET before degradation. Absorption at  $3420\text{ cm}^{-1}$  is the overtone of  $\nu_{\text{C}=\text{O}}$  at  $1710\text{ cm}^{-1}$  for the ester group.  $\nu_{\text{C}-\text{H}}$  of benzene ring occurs at  $3050$  to  $3100\text{ cm}^{-1}$ .  $\nu_{\text{C}-\text{H}}$  of saturated aliphatic hydrocarbons occurs at  $2900$  to  $2980\text{ cm}^{-1}$ . The strong carbonyl absorption occurs at  $1712\text{ cm}^{-1}$ . Benzene ring absorption occurs at  $1500$  to  $1570\text{ cm}^{-1}$ .  $\delta_{\text{H}-\text{C}-\text{H}}$  of the ethylene group occurs at  $1460$  to  $1480\text{ cm}^{-1}$ . Absorption at  $1420\text{ cm}^{-1}$  is due to  $\delta_{\text{C}-\text{H}}$  of benzene ring bending in plane. Absorption at  $1350\text{ cm}^{-1}$  is  $\omega_{\text{C}-\text{H}}$  of wagging for ethylene glycol. Those at  $1240$  to  $1280\text{ cm}^{-1}$  and at  $1105$  to  $1130\text{ cm}^{-1}$  are due to  $\nu_{\text{Ar}-\text{C}(=\text{O})-\text{O}}$  and  $\nu_{\text{C}(=\text{O})-\text{O}}$ , respectively. Absorption at  $745\text{ cm}^{-1}$  is a typical frequency of the interaction between the polar ester and the benzene ring. Fig. 2 shows the difference spectra of PET after various days of accelerated UV irradiation. It is noted that a continuous decrease of absorbances at  $1712$ ,  $1270$  to  $1290$  and  $1135$  to  $1160\text{ cm}^{-1}$  are the result of bond cleavage of ester group and ether linkage. The breakdown of 1,4-disubstituted bonds to the benzene ring was evidenced from the decreased absorbance at  $745\text{ cm}^{-1}$ . These results agree well with reports in literature.

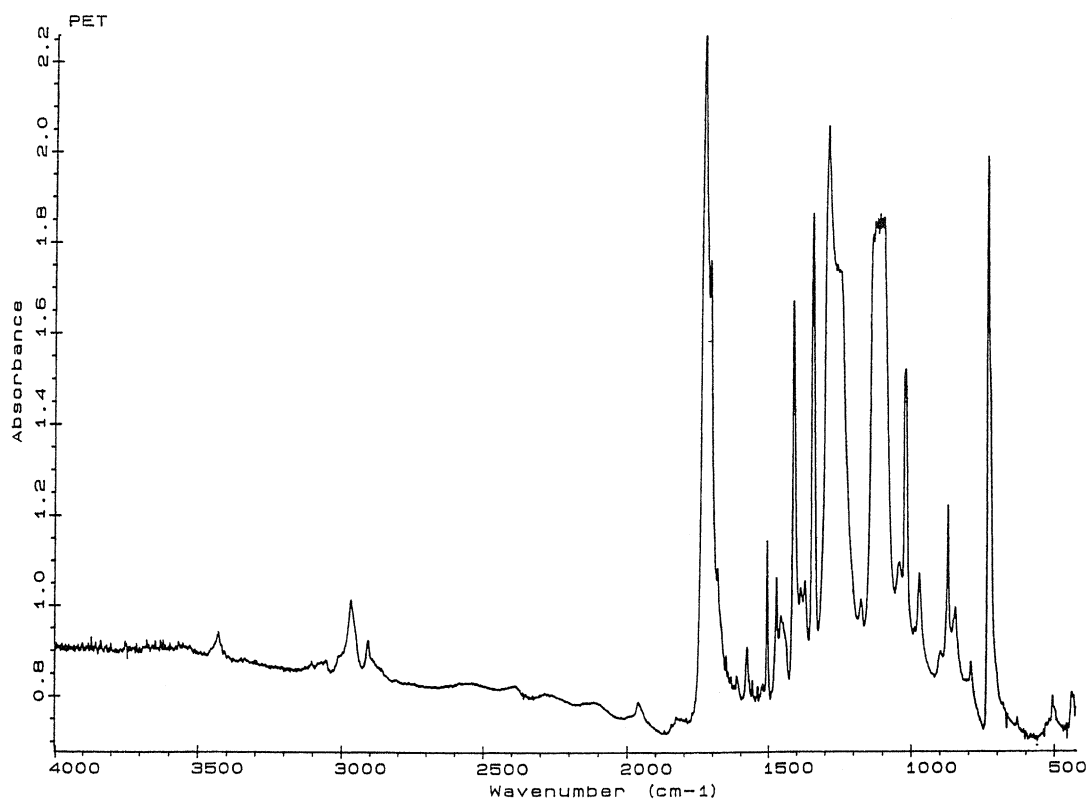


Fig. 1. IR spectrum of PET before photodegradation.

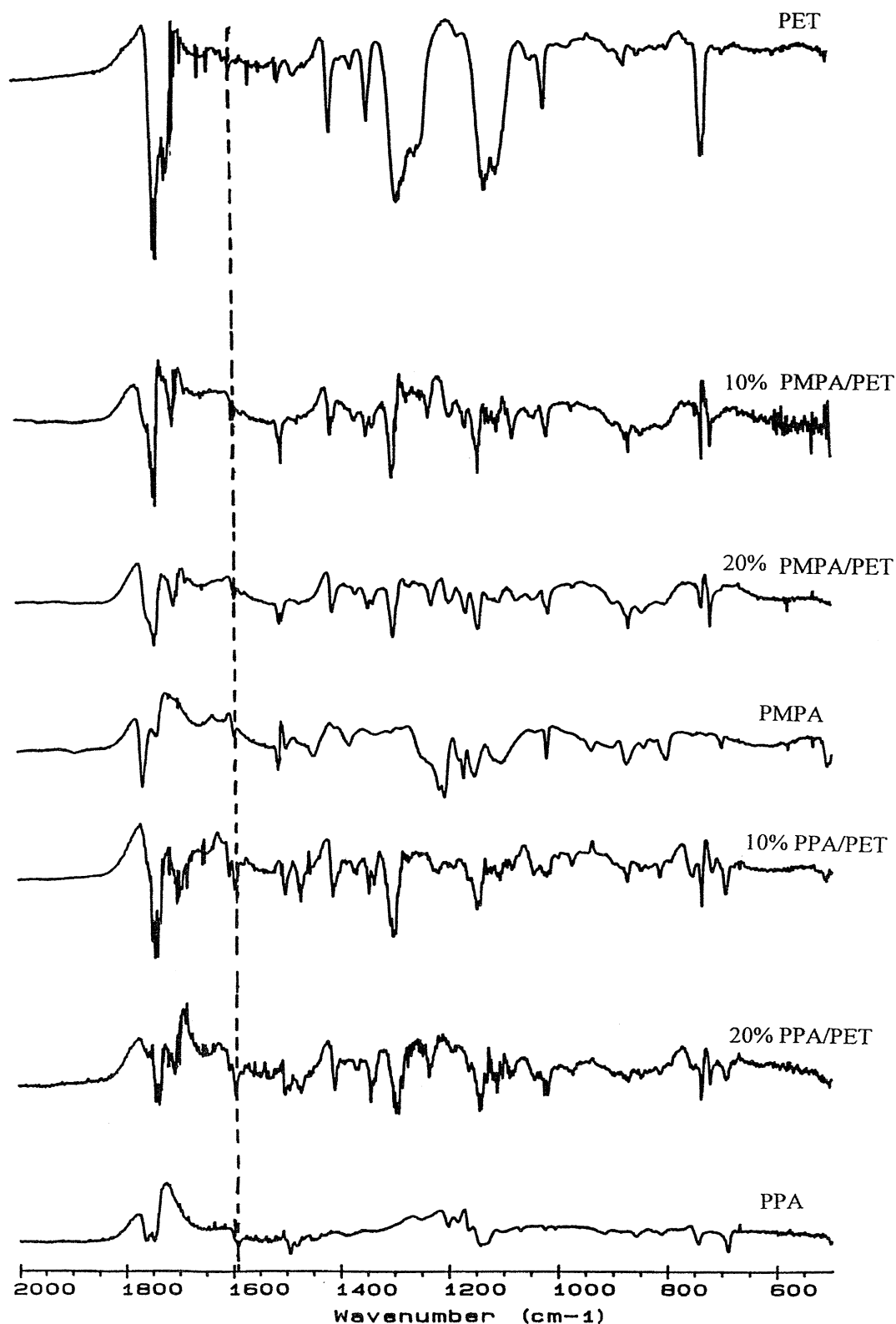


Fig. 2. Typical difference spectra of samples ( $A_6$ – $A_0$ , with benzene absorption as internal standard) after accelerated uv irradiation for 6 days.

Fig. 3 also compares similar difference spectra of films for blends of PMPA/PET (10/90, 20/80), PMPA, PPA/PET (10/90, 20/80) and pure PET after 6 days of UV irradiation. The significant protection of scission at ester

group can be evidenced from the retarded decreases of absorbances at 1712, 1270 to 1290 and 1135 to 1160  $\text{cm}^{-1}$ . Our previous study on the kinetics of photo-Fries' rearrangement for PMPA and PPA indicated that

PMPA produced *o*-hydroxybenzophenone moiety linked to the side chain with a higher rate constant of  $4.53 \times 10^{-6} \text{ s}^{-1}$ , compared with a lower rate constant of  $3.59 \times 10^{-7} \text{ s}^{-1}$  for PPA which produced both *o*- and *p*-hydroxybenzophenone moieties in the side chain (Fig. 3). Of the two products, only *o*-hydroxybenzophenone contains

a 6-membered ring structure with a labile H-bonding between OH and C=O and acts as a UV absorber [1,2]. This implied that PMPA would be a better inherent polymeric photo-stabilizer than PPA. Such a significant stabilization can be attributed to the good compatibility of PET/PMPA and PET/PPA. The miscibility of PMPA

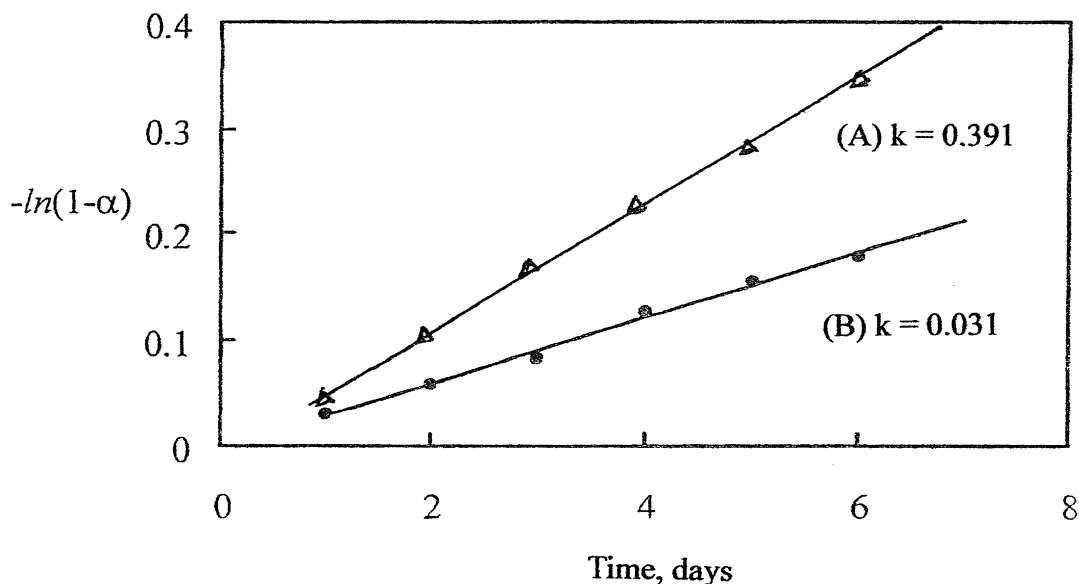


Fig. 3. Plots of first-order rate expression,  $-\ln(1-\alpha)$  vs. time, for PMPA and (B) PPA in photo-Fries' rearrangement, where  $\alpha$  is the conversion.

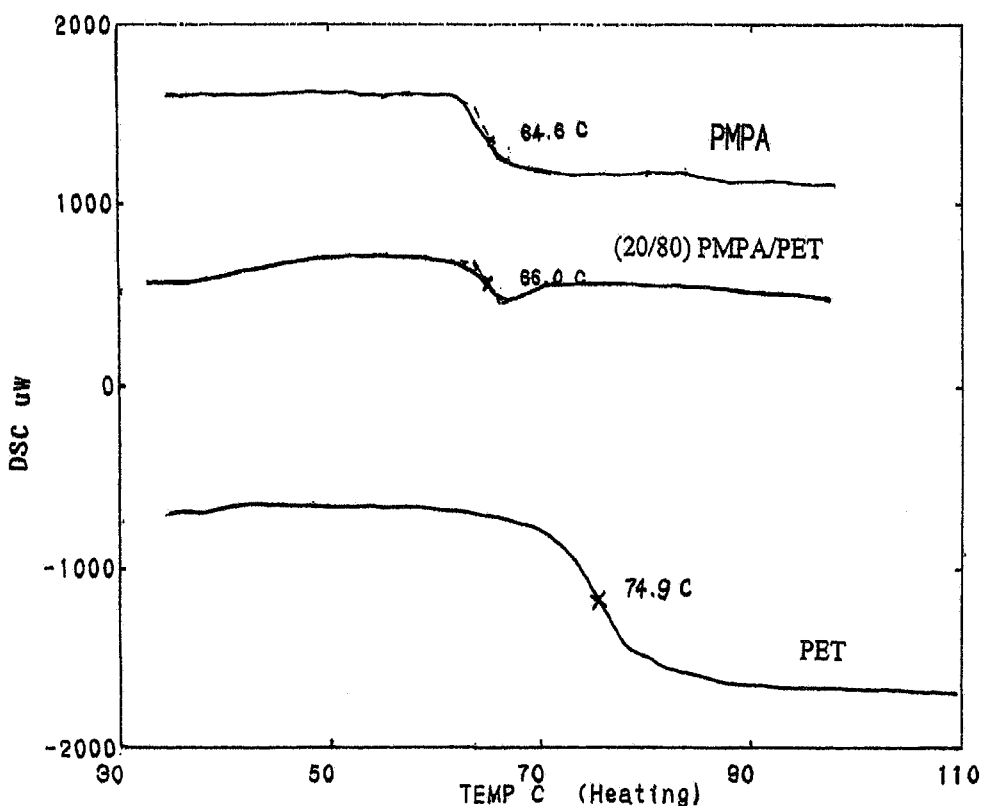


Fig. 4. Comparisons of Tg's for PET, PMPA and PET/PMPA blend.

and PPA in PET in molecular level would provide good protection to PET. Fig. 4 compares the Tg's for PET, PMPA and PET/PMPA blends. PET and PMPA have Tg's of 74.9 and 61.1 °C, respectively. An inner shift of a single Tg at 66.0 °C for the PET/PMPA blend indicates

good compatibility of PET and PMPA. A similar finding was observed for the PET/PPA system (Fig. 5).

Fig. 6 shows the percentage retention of tensile strength for fibres of PET, PET/PMPA (5/95, 10/90), and of PET/PPA (5/95, 10/90) blends after 7 days of

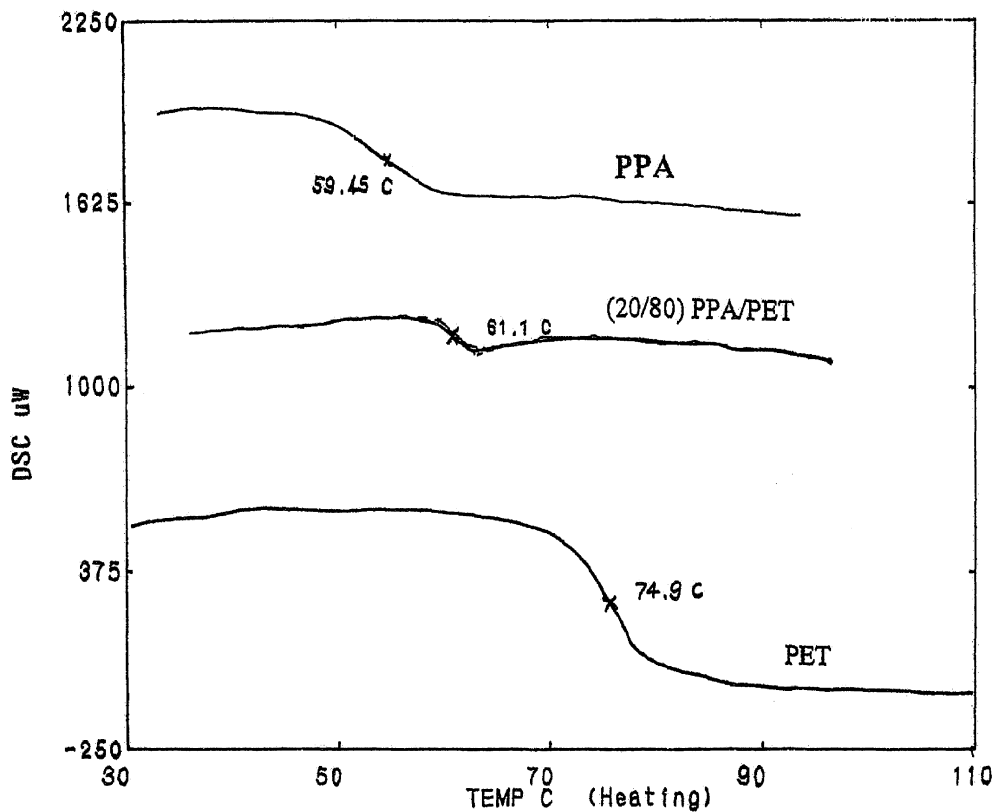


Fig. 5. Comparisons of Tg's for PET, PPA and PET/PPA blend.

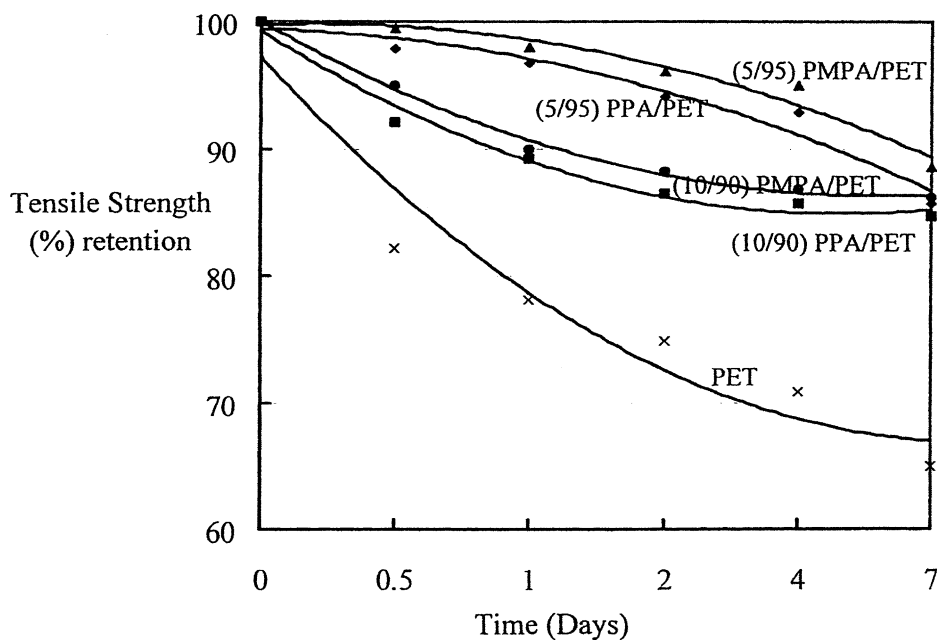


Fig. 6. Percentage retention of tensile strength for fibres of PET, PET/PMPA (5/95, 10/90) and PET/PPA (5/95, 10/90) blends after 7 days of accelerated ageing.

accelerated uv irradiation. It is noted that PMPA conferred more significant photo-stabilization to PET than PPA under the same environment. This experimental result is well consistent with the functional group changes in FTIR monitoring (Fig. 2) and our kinetic study for the photo-Fries rearrangement for PMPA and PPA (Fig. 3). It is noted that fibres of the 10/90 of PMPA/PET and of PPA/PET indicate less retention of tensile strength, presumably because more low molecular weight portions of PMPA and PPA (with an average molecular weight of 9700 and 9600, respectively) in the blends deteriorate the mechanical property.

#### 4. Conclusions

Both PPA and PMPA show good compatibility with PET and indicated significant stabilization of PET fibre against photo-oxidation in an accelerated weathering tester. PMPA indicated better photo-stabilization efficiency because PMPA, upon irradiation of UV, more efficiently produced *o*-hydroxybenzophenone moiety linked to the side chain. Tensile tests of fibres agreed well with functional group changes, as evidenced from FTIR difference spectra and the result of kinetic study. A higher level of low molecular weight PMPA or PPA

incorporated into PET showed an adverse effect on the tensile strength of fibres.

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