MECHANICAL AND MORPHOLOGICAL STUDY OF TALC/CALCIUM CARBONATE FILLED POLYPROPYLENE HYBRID COMPOSITES WEATHERED IN TROPICAL CLIMATES

Y. W. LEONG[1], M. B. ABU BAKAR[2], Z. A. MOHD. ISHAK[3] & A. ARIFFIN[4]

Abstract. Two kinds of composites, namely single-filler polypropylene (PP) composites (contain either talc or calcium carbonate) and hybrid-filler PP composites (consist of a mixture of talc and calcium carbonate) were injection moulded into dumbbells. These specimens were subjected to natural weathering i.e. tropical climate in Penang, Malaysia for 6 months. After 6 months of exposure, the mechanical properties of single-filler PP composites deteriorated due to severe physical and chemical degradation. This was confirmed after studies were made on the structure aspects of the composite. However, the hybrid-filler PP composites were found to show better retention in both tensile and flexural strength albeit have undergone some degree of degradation as well. It was found that the 'hybridization' effect has successfully increased the resistance of the hybrid composite to severe environmental degradation to the extent that it protects the internal structure of the composite from environmental damage, while the surface of the composite gets severely degraded.

Keywords: Polypropylene, hybrid composite, photooxidation, chain scission, thermal degradation, natural weathering

Abstrak. Dua jenis komposit, iaitu komposit poli propilena (PP) terisi-tunggal (diisi dengan talkum atau kalsium karbonat) dan komposit PP terisi-hibrid (diisi campuran talkum dan kalsium karbonat) yang telah diacuan-suntikkan kepada bentuk 'dumbbell'. Spesimen tersebut didedahkan kepada pencuacaan semulajadi, iaitu iklim tropika di Pulau Pinang, Malaysia selama 6 bulan. Selepas tempoh pendedahan, sifat mekanikal PP terisi-tunggal telah merosot akibat degradasi fizikal dan kimia yang teruk. Kajian yang lebih mendalam ke atas aspek struktur komposit telah dijalankan untuk mendapatkan kepastian tentang keadaan degradasi tersebut. Walau bagaimanapun, komposit PP-terisi hibrid menunjukkan keupayaan untuk mengekalkan sifat tegangan dan lenturan yang lebih baik walaupun terdapat kesan degradasi pada permukaan spesimen. Didapati bahawa kesan '*hibridisasi*' telah berjaya meningkatkan ketahanan komposit hibrid terhadap degradasi pencuacaan yang teruk, sehingga struktur-struktur di dalam komposit tersebut dapat dilindungi daripada kesan degradasi, sedangkan permukaan komposit telah mengalami degradasi yang teruk.

Kata kunci: Polipropilena, komposit hibrid, pengoksidaan-foto, pengguntingan rantai, degradasi terma, pencuacaan semula jadi

---

[1,2,3&4]School of Materials & Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia.
[1] Correspondence e-mail: leongyewwei@hotmail.com

1.0   INTRODUCTION

Polypropylene (PP) composite is one of the most extensively produced polymers, especially widely used as automotive parts [1]. In outdoor applications all polymers degrade. Many of those parts, having been exposed to sunshine for long periods of time, are heavily photo-oxidized due to the relative high photosensitivity of PP; hence changes are expected in the thermal behaviour, mechanical properties and morphology of the products.

Although studies on the effect of natural weathering, thermal oxidation and degradation on isotactic and virgin PP has been covered extensively in various literatures [2-7], similar publications that involve composites, especially hybrid composites that combine two or more different types of fillers, are extremely limited. In this work, the influence of natural weathering on the mechanical, morphological, and crystallinity of talc and calcium carbonate ($CaCO_3$) filled PP hybrid composites will be reported. Talc and $CaCO_3$ were chosen, as they are the most widely used fillers in automotive applications, which are also subjected to environmental exposures. All composites studied are based on 30 wt% filler loading due to the fact that 30 wt% talc-filled PP was proven to have ultimate strength in a previous study [8], which was subsequently used as a benchmark for this study. Injection-moulded dumbbells of this composite with varying compositions of talc and $CaCO_3$ were weathered outdoors in Penang, Malaysia with exposure times varying from 2 to 6 months. The investigation began initially as part of an extensive study and characterisation of the mechanical, thermal, flow and morphological properties of talc and $CaCO_3$ filled PP hybrid composites. The results of treating the composites with UV stabilisers and anti-oxidants provide valuable information that assists the interpretation of natural weathering trials and helps to identify the importance of climatic aspects that are often not given adequate consideration. The crystallisation and melting behaviour of degraded polymer was studied by differential scanning calorimetry (DSC) while the morphology of the samples was studied under scanning electron microscope (SEM). Mechanical testing such as tensile, flexural and impact tests were also done to determine the physical aspects of the composites.

2.0   EXPERIMENTAL PROCEDURE

2.1   Sample Preparation

Polypropylene copolymer grade Pro-Fax SM240 with melt index of 25 g/10 min was used. The density of the polymer is 0.894 g/cm^3. The filler particles consist of talc and calcium carbonate ($CaCO_3$). Two grades of $CaCO_3$ were used, one was untreated (UCC) and the other treated with stearic acid (TCC) by the manufacturer. The details of the fillers are listed in Table 1. Other additives include an anti-oxidant Irganox 1010 and ultra-violet stabilizer Tinuvin 770 DF.

Table 1   Material specification

Materials	Density (g/cm^3)	Specific surface area (m^2/g)	Mean particle diameter (mm)
Talc (T)	2.79	1.50	6.3
Untreated CaCO$_3$ (UCC)	2.70	3.57	3.3
Treated CaCO$_3$ (TCC)	2.70	3.58	3.2

The various composite formulations that were used in the study are shown in Table 2. The first three formulations (T30, UCC30 and TCC30) are single filler PP composites whereas the remaining formulations (T15:UCC15 and T15:TCC15) are PP hybrid composites.

Table 2   Composite composition according to weight percent (wt%) of each component

Sample code	Wt% PP	Wt% Talc	Wt% Untreated CaCO$_3$	Wt% Treated CaCO$_3$
T30	70	30	–	–
UCC30	70	–	30	–
TCC30	70	–	–	30
T15:UCC15	70	15	15	–
T15:TCC15	70	15	–	15

Compounding was carried out with a twin-screw extruder (model Haake Rheomex CTW 100). The barrel temperatures of four zones were between 160°C and 190°C from feeding to die zones. Compounds were blended at a screw speed of 25 rpm. The extrudates were cooled in a water bath, pulled and pelletised. Dumbbell test specimen were injection moulded in a tensile mould using a 35-ton Battenfeld BA 350 CD machine with a Unilog 4000 control system. The injection moulding barrel temperature ranges from 190 to 230°C while the back pressure is 350 bar.

2.2   Weathering Test

The mean temperature and total rainfall in Penang, Malaysia was compiled for each month according to the data obtained from Penang Weather Station, and plotted in Figures 1 and 2 respectively. The weathering period was from October 2001 to March 2002.

The weathering test was conducted according to ASTM D1435. Specimens were attached to a rack with a rack holder. The rack was adjusted to face the equator at an
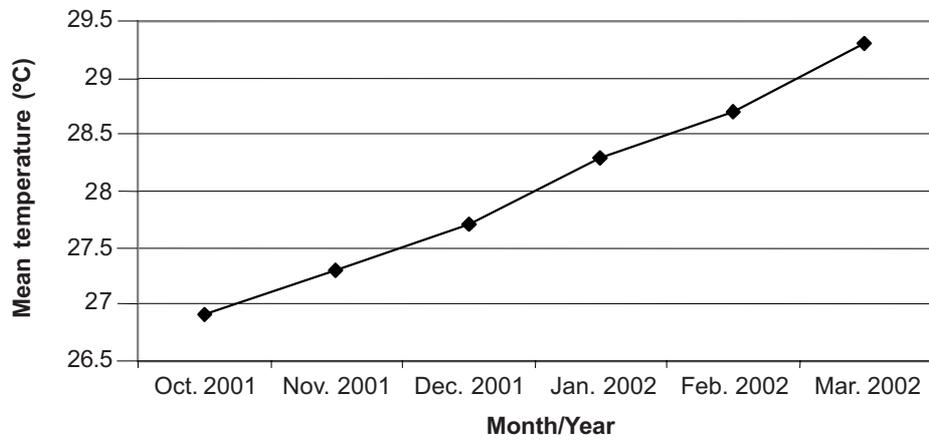
Figure 1   Mean Temperature For Each Month From October 2001 to March 2002
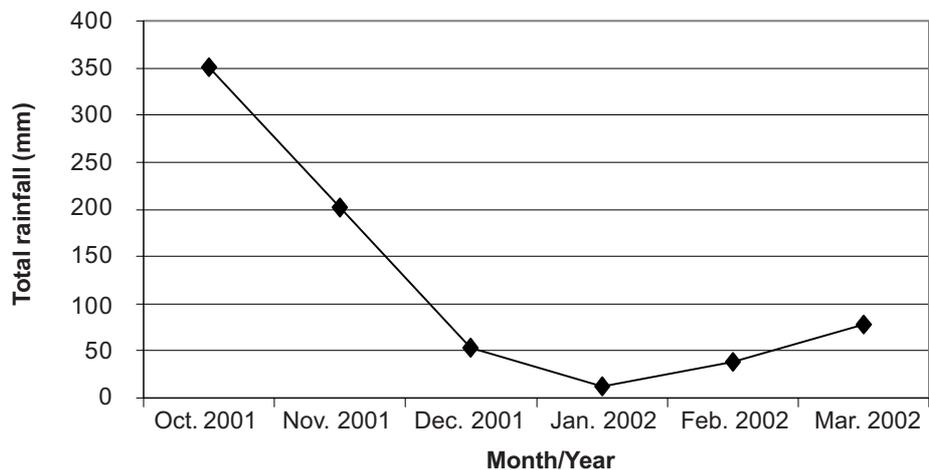
Figure 2   Total Rainfall For Each Month From October 2001 to March 2002

angle of 45°C. The rack is situated at an open area whereby it is free from being overshadowed by other objects. The specimens were exposed to all environmental effects such as rain, sunlight, wind, etc. Samples were collected every two months to determine the degree of degradation. Moisture at the surface of the samples were removed with a clean towel and left in the air for 24 hours at room temperature before mechanical tests were conducted.

2.3   **Mechanical and Structural Property Measurements**

Tensile and flexural properties were measured using a Testometric tensile machine, model M500-25 kN in accordance with ASTM D638 and ASTM D790-86 using Type

1 test specimen dimensions. For tensile tests, a crosshead speed of 5 mm/min was employed and the average value of at least five specimens were taken for each sample. For flexural tests, a three-point loading system was used and support span length was adjusted to 50 mm. The crosshead speed was 3 mm/min. All tests were carried out in an air-conditioned room (27°C).

The mode of fracture was studied by analysing the fracture surface of tensile samples. This was carried out using scanning electron microscopy (SEM) machine, Model Leica Cambridge S-360 where the fracture surface of the tensile test specimens was coated with a thin gold layer to avoid electrical charge accumulation during examination.

3.0   RESULTS AND DISCUSSION

### 3.1   Effect Of Natural Weathering On Mechanical Properties

Figure 3 shows the comparison of tensile modulus between single filler PP composites with hybrid filler PP composites. A significant increase in modulus can be seen in all formulations regardless of single-filler or hybrid-filler composites. The increase in modulus for T30, T15:UCC15 and T15:TCC15 accounted for about 39% whereas an increase of about 46% was recorded for UCC30 and TCC30 after 6 months of exposure. The increase in modulus is due to the effect of photodegradation, which occurs when the composites were exposed to both oxygen and sunlight [9]. Photodegradation causes chain scission to occur in the amorphous regions of the polymer, which changes the balance between brittle and plastic flow, thus dramatically reduces the ductility of the composites. This chain scission will also lead to restructuring, increased crystallinity, and eventually surface cracking.
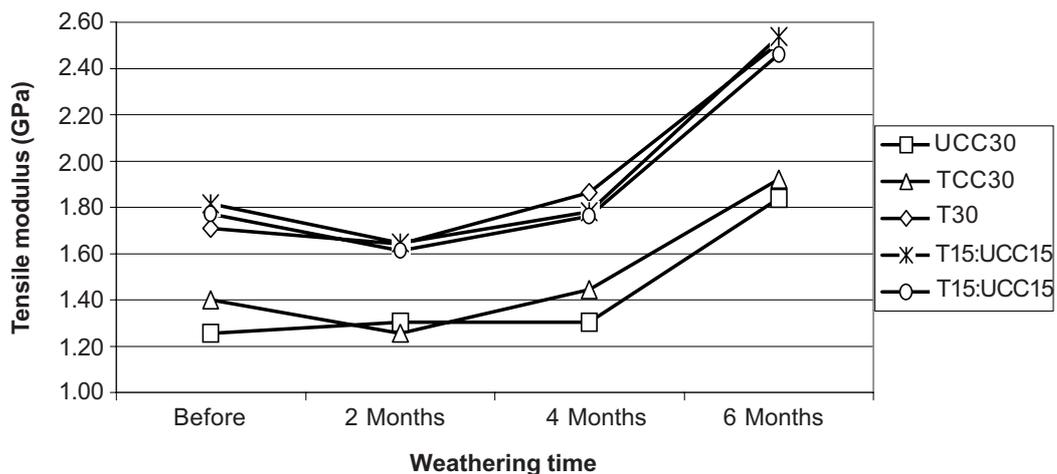

Figure 3   Tensile modulus of single-filler and hybrid-filler PP composites

The tensile stresses of the composites are also expected to decrease due to the formation of surface cracks, which act as stress concentration points. However this was only true for the single-filler composites after 6 months of exposure, as can be seen in Figure 4. A drastic decrease for UCC30 followed by TCC30 can be attributed to the fact that both composites were filled with different grades of $CaCO_3$, which was proven earlier to be non-reinforcing filler [1]. The decrease in tensile strength is minimal for talc-filled PP (only about 6%) due to the fact that it is a reinforcing filler, which might be able to tolerate the devastating effects of weathering. Interestingly, both hybrid-filler composites were seemingly not susceptible to the effects of weathering, the change in tensile strength for both composites were negligible. In these hybrid-filler composites there are two different kinds of filler particles that have different characteristic advantages, which can compensate on the weaknesses of each other. For instance, talc, which is platy in nature, will act as the main reinforcing filler. On the other hand, $CaCO_3$, being spherical in shape and non-reinforcing will cause the formation of interparticle ligaments following particle-matrix debonding [10]. These ligaments would act as "dampers" which can absorb energies from propagating cracks before it reaches the parts where talc is holding the composite together. This 'hybridisation' effect could not have happened in single-filler composites, thus explaining the retaining of tensile strength for the hybrid-composites in Figure 4.
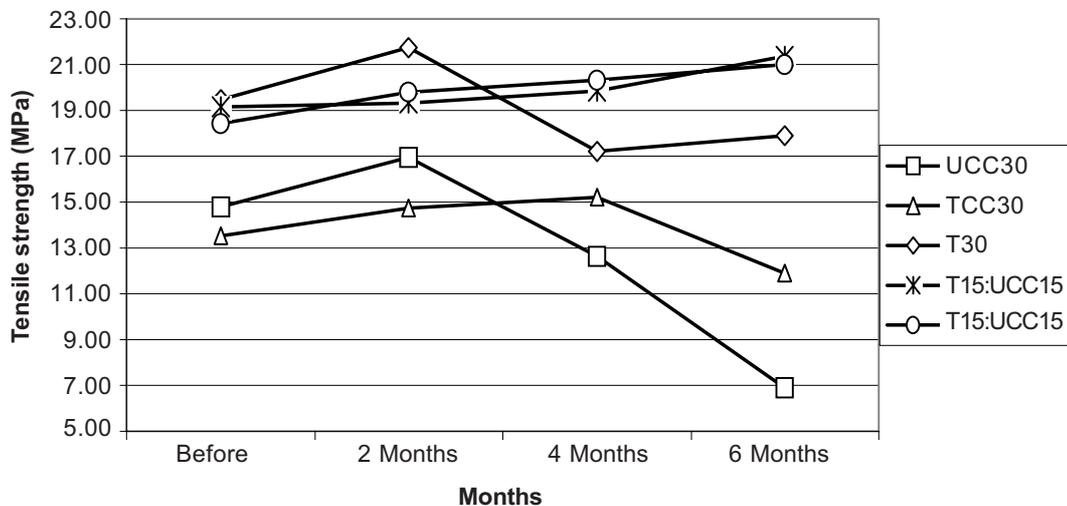
Figure 4   Tensile strength for single-filler and hybrid-filler PP composites

As expected, the elongation at break for all composites decreased over a period of 6 months exposure as can be seen in Figure 5. The long exposure period especially in an urban area such as Penang could cause the build up of polynuclear aromatic compounds at the surface of the samples due to urban pollution [9]. This, combined with hydroperoxides as well as carbonyl groups that might form during compounding,
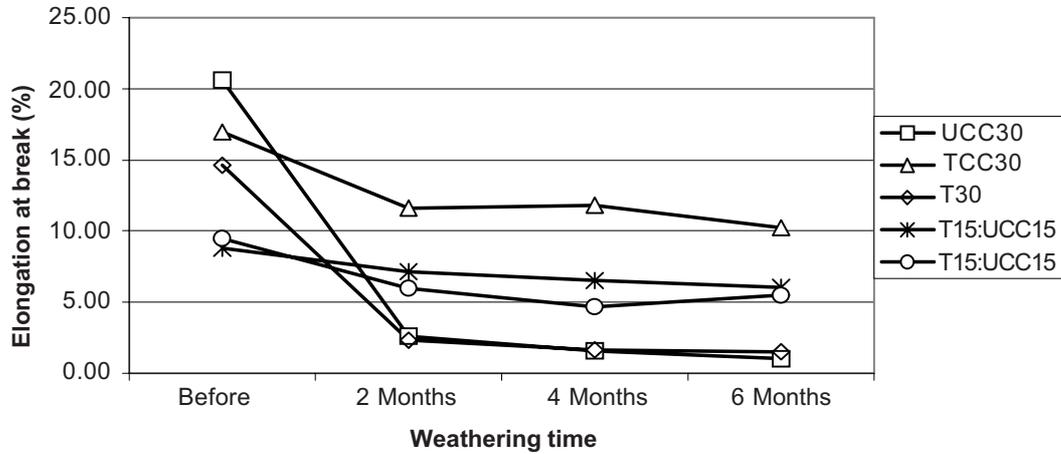
Figure 5   Elongation at break for single-filler and hybrid-filler PP composites

could also be the main reason that causes the embrittlement of the composites. Stress concentration points caused by formation of surface cracks also favours crack propagation rather than ductile yielding as the dominant failure mechanism.

The increase in flexural modulus during the initial periods of weathering of 2 months as illustrated in Figure 6, can also be attributed to the increased brittleness and stiffness of the composite caused by photo-oxidation. Photo-oxidation is only concentrated near the surface of the samples since oxygen is used up before it can diffuse to the interior. The photo-oxidation process takes place mainly in the amorphous region because of the higher permeability to oxygen and also due to the rejection of chromophore impurities by the growing crystals [11]. However, longer exposure times causes the development of more and more surface cracks, which in turn allows chemical degradation and water absorption to take place.
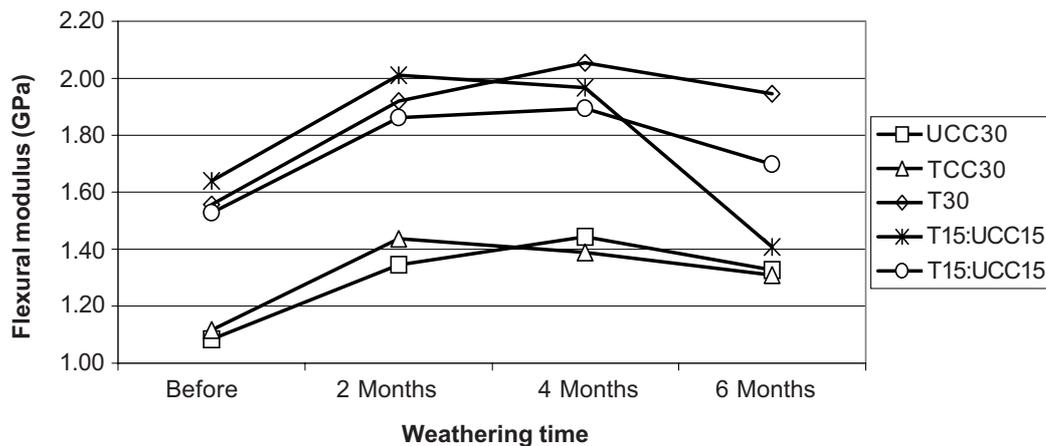
Figure 6   Flexural modulus for single-filler and hybrid-filler PP composites

Water absorption and chemical degradation can be caused by exposure of the composite to acidic rainwater and moisture, which can seep through the crevices of the surface cracks, causing chemical attack to the polymer bonds [12]. Therefore, the application of flexural stress, as compared with tensile stress, can be more detrimental to the flexural modulus of the composites that were exposed for more than two months, which is why the increment of flexural modulus is very low for most samples (about 18 to 26%). The only sample which records a drop in flexural modulus is T15:TCC15 after 6 months of exposure.

Similar to tensile strength, the reduction in flexural strength of most single-filler PP composites was recorded as illustrated in Figure 7. A very nominal increase in flexural strength, which could be negligible, was recorded for samples TCC30, T15:UCC15, T15:TCC15. The reason for the retaining of flexural strength for the hybrid composites is similar to the reasons discussed for the retaining of tensile strength. As for TCC30, the flexural strength could be retained due to better dispersion of the filler since stearic acid has been known to be a dispersing agent [1]. A better dispersion of fillers will inevitably strengthen matrix-particle bonding, thus titrating the effects of weathering.
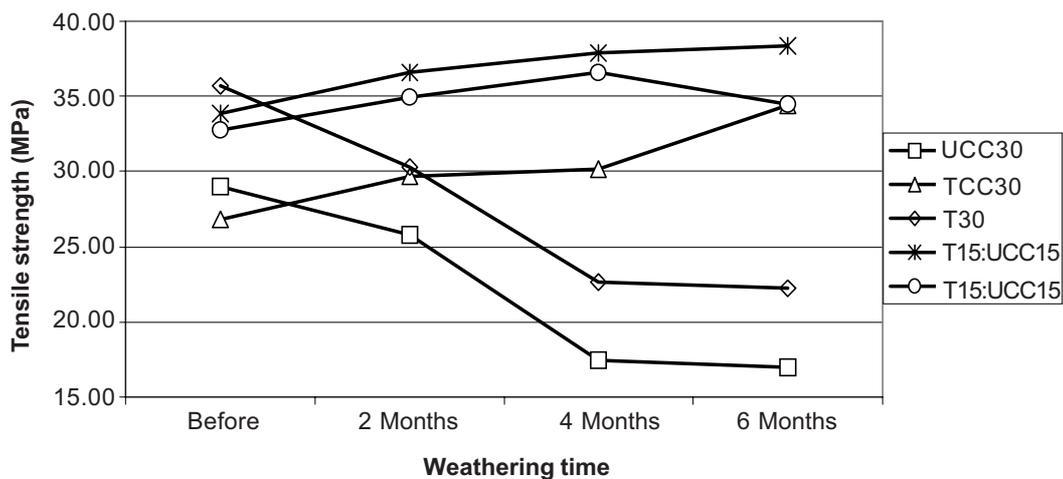

**Figure 7**   Flexural strength for single-filler and hybrid-filler PP composites

3.2   Effect Of Natural Weathering On Morphology

Figure 8(a,b,c,d,e) shows the exposed surfaces of various compositions after 6 months of exposure. Although surface cracks are evident in all samples after being weathered for 6 months, the severity of the cracks varies from one another.

Surface cracks form spontaneously during UV exposure as the result of the increase in crystallinity at the surface layers, which lead to shrinkage [9]. It can be seen that the surface of UCC30 has severely deteriorated with large, continuous surface cracks, as
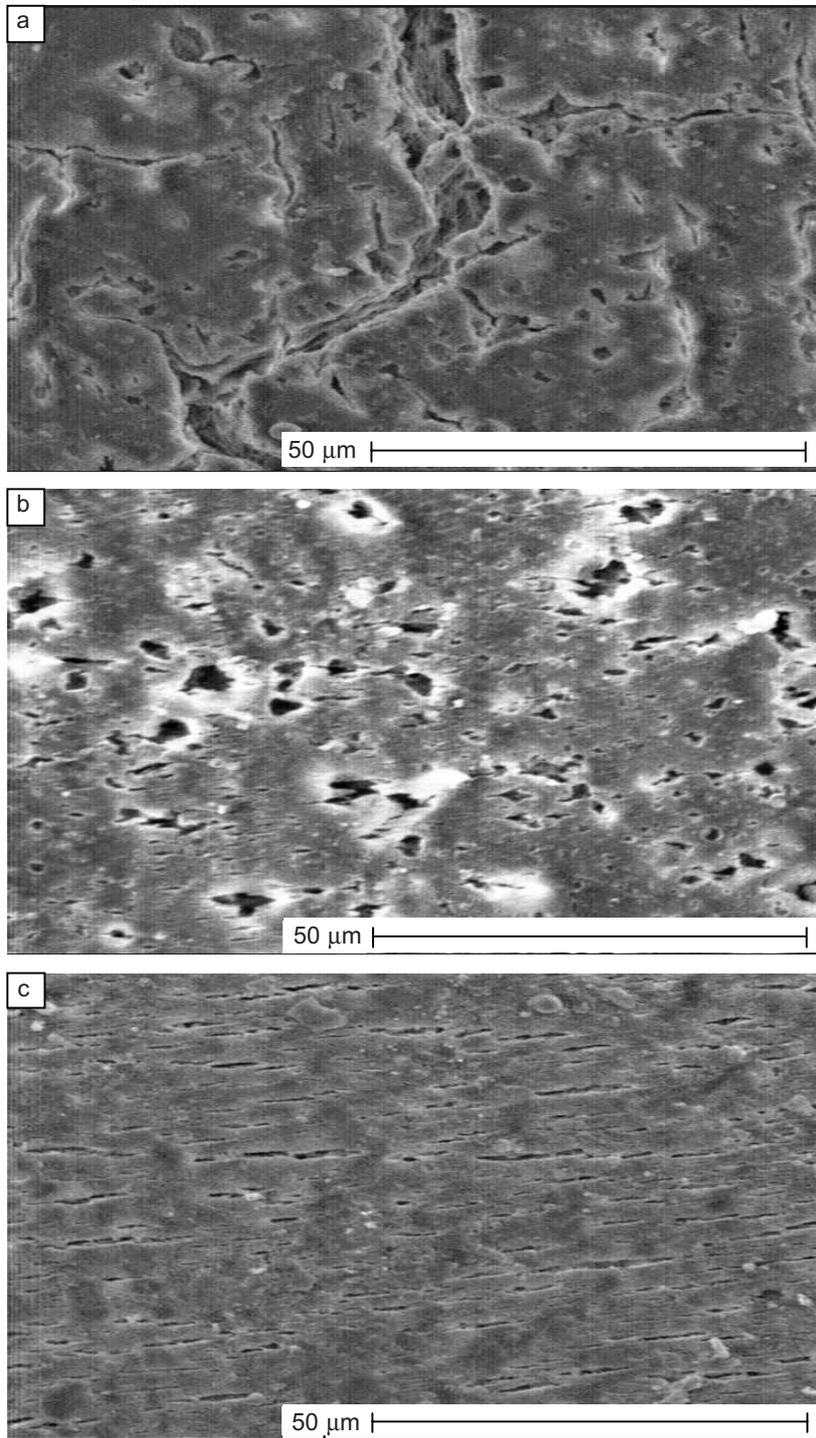
Figure 8   Surface aspects of different compositions after 6 months of exposure.
(a) UCC30; (b) TCC30; (c) T30; (d) T15UCC15; (e) T15TCC15.
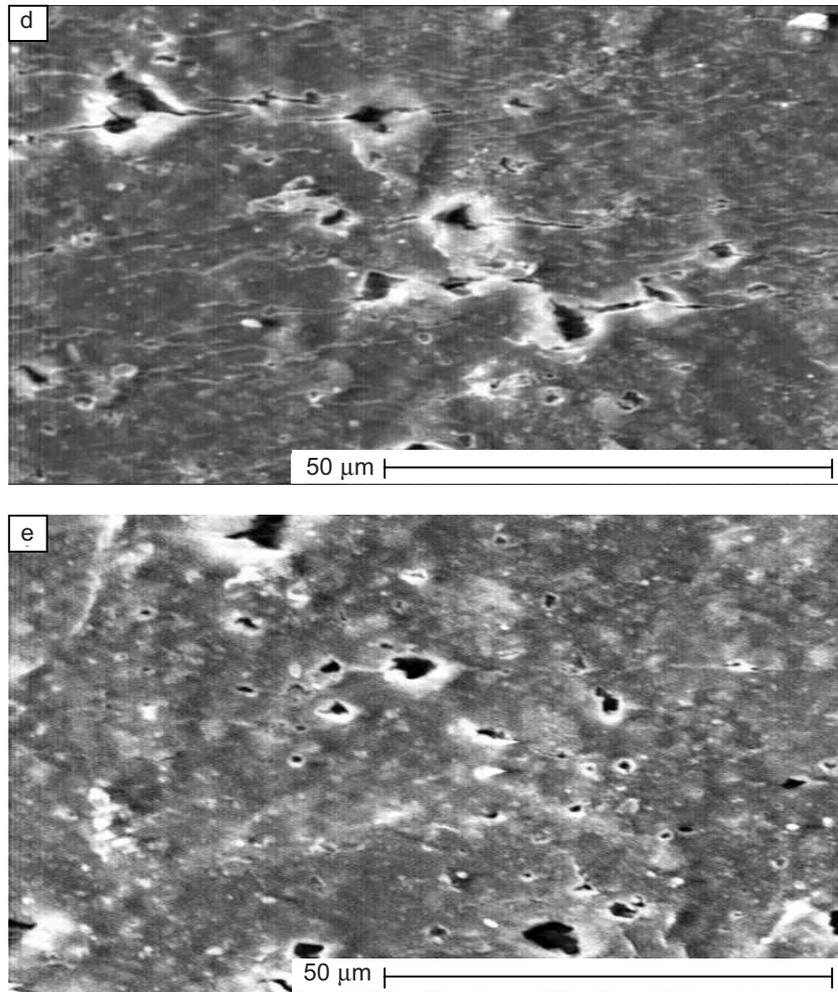
Figure 8 Surface aspects of different compositions after 6 months of exposure. (a) UCC30; (b) TCC30; (c) T30; (d) T15UCC15; (e) T15TCC15. (*Cont*.)

well as smaller diamond shaped cavities. The extent of deterioration for TCC30 is also quite severe; judging by the high concentration of large size diamond shaped cavities, although very few continuous surface cracks are present. As for T30, small surface cracks are widely spread throughout the surface of the composite. The least damage done by weathering is on samples T15:UCC15 and T15:TCC15 that contain very few cracks and only localised diamond cavities. Rabelo and White [11] suggested that for surfaces that are not severely deteriorated, the cracks initiated at the surface are arrested at this site and the ultimate failure is determined by the interior properties of the composite. The existence of this feature may be responsible for the better retention of tensile and flexural strength for both T15:UCC15 and T15:TCC15 compositions (*see* Figures 4 & 7).

4.0 CONCLUSION

The degradation of a composite material due to exposure to the environment does not necessarily have detrimental effects to the mechanical properties of composite. The trend observed for the effect of structure and morphological properties on the extent of chemical and photo degradation of PP composites is not always reflected in the mechanical behaviour. This is because the mechanical properties of photo degraded PP composites may depend also on other features such as spherulites size, the presence of surface cracks, filler particle size, particle orientation and the specimen thickness. Therefore, it is important to recognise that the knowledge in chemical and photo degradation may not be sufficient to predict the deterioration in mechanical properties. Exposure time and photodegradation kinetics play a vital role in determining the degree of degradation of a polymer composite, whereby in this study, the exposure time for hybrid composites was not sufficient to cause degradation to the internal parts of the composite. Moreover, the synergistic effects of hybrid fillers to counter the effects of weathering are evident whereby the fillers work hand in hand to compensate the weaknesses of each other, thus making the hybrid composite less susceptible to environmental degradation as well as mechanical stresses as compared with single-filler composites. The higher rate of degradation experienced by single-filler composites is due to the fact that the filler succumbed to its individual weaknesses. For instance, although talc provides strength to the surrounding PP matrix, it has no dampening effect during the propagation of surface cracks because there was no formation of interparticle ligaments as in $CaCO_3$-filled PP composites. On the contrary, $CaCO_3$ does not reinforce the matrix, thus the decrease in tensile and flexural strength is absolutely normal.

REFERENCE

[1]   Pukanszky, B. 1995. Particulate Filled Polypropylene: Structure and Properties. In J. Karger-Kocsis ed. *Polypropylene: Structure, Blends and Composites*. London: Chapman and Hall. 3: 1-70.

[2]   Teissedre, G., J. F. Pilichowski, S. Commereuc and J. Lacoste. 1996. "Photoageing of Polyolefins. II: Photolysis of Molecular Weight Ketones at λ> 300 nm". *Polymer Degradation & Stability*. 51: 143-150.

[3]   Geuskens, G. and G. Nedelkos. 1996. "The Post-irradiation Oxidation of Polypropylene. II: Influence on the Mechanical Properties". *Polymer Degradation & Stability*. 51: 223-225.

[4]   Grossetete, T., L. Gonon and V. Verney. 2002. "Submicrometric Characterization of the Heterogeneous Photooxidation of Polypropylene by Microthermal Analysis". *Polymer Degradation & Stability*. 78: 203-210.

[5]   Gijsman, P., M. Kroon and M. van Oorschot. 1996. "The Role of Peroxides in the Thermooxidative Degradation of Polypropylene". *Polymer Degradation & Stability*. 51: 3-13.

[6]   Czegeny, Z. S., E. Jakab, A. Vig, B. Zelei and M. Blazso. 2000. "Thermal Decomposition of Photooxidized Isotactic Polypropylene". *Journal of Analytical and Applied Pyrolysis*. 56: 229-242.

[7]   Girois, S., L. Audouin, P. Delprat and J. Verdu. 1996. "Weight Loss Mechanism in the Photooxidation of Polypropylene". *Polymer Degradation & Stability*. 51: 133-141.

[8]   Leong, Y. W., M. B. Abu Bakar, Z. A. Mohd. Ishak and A. Ariffin. 2003. "Comparison of Mechanical Properties and Interfacial Interaction Between Talc, Kaolin and Calcium Carbonate Filled Polypropylene Composites". *Journal of Applied Polymer Science*. submitted for publication.

[9] Allen, A. S. 1983. *Degradation and Stabilization of Polyolefins*. Applied Science Publishers.

[10] Thio, Y. S., A. S. Argon, R. E. Cohen and M. Weinberg. 2002. "Toughening of Isotactic Polypropylene with $CaCO_3$ Particles". *Polymer*. 43: 3661-3674.

[11] Rabello, M. S. and J. R. White. 1997. "The role of Physical Structure and Morphology in the Photodegradation Behaviour of Polypropylene". *Polymer Degradation & Stability*. 56: 55-73.

[12] Davis, A. and D. Sims. 1983. *Weathering of polymers*. Applied Science Publishers.