UV Aging Behavior of Functionalized Mullite Nanofiber-Reinforced Polypropylene
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ABSTRACT: In this study, the effect of accelerated ultraviolet (UV) aging on the properties of polypropylene (PP) as well as its blend with PP-graft-maleic anhydride (PP-g-MA) and composite with amine-functionalized mullite nanofibers (AMNF) was compared. Solid-state NMR exhibited some changes in the macromolecular chain structure after aging, whereas the formation of degradation products was confirmed through Fourier transform infrared (FTIR) spectroscopy. The aged composite was observed to exhibit the least increment in the crystallinity from X-ray and differential scanning calorimetry (DSC) analyses (0.3 and 0.5%, compared to 9.7 and 10.4%, respectively, for PP) owing to the stability of its amorphous phase against degradation. Similar resistance toward degradation was also confirmed by thermogravimetric analysis (TGA). The surface morphology of the materials also exhibited the lowest extent of surface embrittlement as well as a small number of shallow cracks in the case of a-PP/PP-MA and composite with AMNF composite. The aged composite had a much higher impact strength of 14.9 kJ m$^{-2}$ compared to 2.5 kJ m$^{-2}$ for aged PP, thus exhibiting its stability against degradation owing to a synergistic combination of the filler and compatibilizer. The optimal performance of the composite was further confirmed through the least extent of reduction in the tensile strength and elongation at break. These findings demonstrate the superior performance of AMNF-reinforced PP composite over PP for outdoor applications.

1. INTRODUCTION
Excellent property profiles and processability enable the polymeric materials to replace other conventional materials in application areas such as aerospace, automobiles, marine infrastructure, building and construction, etc. In the case of outdoor applications, the overall performance of the polymeric materials greatly depends on their behavior toward various environmental factors including ultraviolet (UV) light, variations in temperature and moisture, pollutants, presence of oxygen and ozone, biological attack, mechanical stresses, etc.1–4 Lifetime predictions of the polymers provide an idea about their durability, maintenance, and replacement and are necessary for all kinds of outdoor applications. Commonly, the weatherability of the materials can be anticipated using the laboratory-accelerated aging testing with the help of artificial light sources such as xenon long arc, fluorescent UV, metal halide or carbon arc lamps, etc. The molecular impact of accelerated aging on the microscopic and macroscopic properties of polymers can be used to predict their weathering resistance under natural use conditions.3,5,6 Photodegradation of polymers is an irreversible process in which UV light decays their properties in the presence of other accelerating factors such as temperature, humidity, and air pollutants. The extent of interaction of polymeric materials with UV light is the key factor determining the rate of photodegradation.3–11 The influence of UV radiation generally leads to two structural changes in the polymeric materials: chain scission and cross-linking. Chain scission upon UV aging can result in decreased molecular weight and increased crystallinity with the evolution of more carboxylic acid and vinyl groups, whereas cross-linking generates increased molecular weight without affecting the crystallinity of the materials.5,7–11
Polymer nanocomposites are functional materials generated by reinforcing polymers with a variety of nanofillers such as nanoparticles, nanorods, nanoplatelets, nanolakes, nanofibers, etc. These materials offer superior mechanical, electrical, thermal, and gas barrier properties compared to pure polymer matrices due to nanoscale filler dispersion.12–14 Among many polymers employed to generate polymer nanocomposites, a significant research effort has been devoted to the development of polypropylene (PP) composites to overcome its limitation of low impact resistance at low temperatures.15,15–19 Mullite is
one of the ceramic nanomaterials with its structure combining silica and alumina (3Al₂O₃/2SiO₂), and it is widely used in electronic, optical, and high-temperature structural applications. In addition, mullite can be used in packaging materials and memory devices. Recently, mullite nanofibers (MNF) have been used as a nano filler for the development of epoxy, unsaturated polyester resin, and polypropylene nanocomposites due to their high thermal stability, optimal oxygen resistance, and low dielectric constant.

Analysis of the UV aging performance of polymer nanocomposites is vital to widen their engineering applications under external environmental conditions. In this respect, photooxidation of PP/clay and PP-graft-maleic anhydride (PP-g-MA)/clay nanocomposites containing 5 wt % filler was evaluated by Tidjani and Wilkie using UV irradiation at ℓ < 300 nm and 50 °C. The unsuitability of clay toward the photostability of PP was observed, and the disappearance of the photodegradation induction period of the nanocomposites confirmed their faster photodegradation than PP. Mailhot et al. also reported similar chemical changes and photodegradation behavior of PP-g-MA compatibilized PP/organically modified montmorillonite nanocomposites. Bocchini et al. studied the photooxidation of PP nanocomposites comprising unmodified and organically modified nanoboehmite at 60 °C with ℓ > 300 nm. The presence of unmodified boehmite in the PP matrix reduced its photooxidation induction period, which was attributed to the adsorption of the phenolic antioxidant present in PP on the hydrophilic polar boehmite surface. In another study, Bocchini et al. reported a similar oxidation induction time (OIT) reduction behavior for PP-g-MA compatibilized PP/hydrrotalcite nanocomposites compared to pristine PP. Also, the photostability recovery of the solvent-extracted PP-based nanocomposites was reported. Furthermore, the authors observed the photooxidation acceleration effect due to the transition metal present as impurity in nanohydrrotalcite. Alongi et al. investigated the role of β-cyclodextrin nanosponges (NS) in the UV-accelerated aging of PP in combination with UV stabilizers such as 2-hydroxy-5-(octyloxy)-benzophenone (HOBP) and triphenyl phosphite (TPP). PP/NS nanocomposites presented an increase in absorbance at hydroxyl (2723 cm⁻¹) and carbonyl (1717 cm⁻¹) infrared regions. It was observed that the incorporation of NS alone in PP reduced its OIT from 12 to 8 h during UV aging. To the best of our knowledge, the UV aging behavior of the PP/MNF nanocomposites has rarely been analyzed. As these composites represent a vital class of materials with immense commercial potential, it is important to gain insights into their UV degradation behavior so as to ascertain the effective service life and performance in outdoor applications. Thus, in this study, the effect of UV aging on the thermal, mechanical, and morphological properties of the PP/PP-g-MA/amine-functionalized MNF (AMNF) has been studied in detail.

2. RESULTS AND DISCUSSION

Figure 1a–c presents the rheological properties of the unaged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF samples. The addition of PP-g-MA resulted in a decreased modulus and viscosity of PP due to matrix plasticization. The incorporation of the covalently bonded PP-g-MA/one-dimensional (1-D) AMNF hybrid to the PP matrix also exhibited reduced modulus and viscosity; however, the magnitude of reduction was smaller compared to PP-g-MA. It indicated that the
rheological performance of the composite evolved from the competing factors of matrix reinforcement due to filler addition and matrix plasticization due to the addition of PP-g-MA. Owing to their morphology, the 1-D particles did not significantly alter the flow behavior of the polymer. Thus, the composite could be processed under the same conditions as the pure matrix, which represents an important requirement for commercial applications. Figure 1d also presents the morphology of the PP/PP-g-MA/AMNF composite. The filler phase was observed to be uniformly distributed in the polymer matrix without any significant aggregation. Thus, the chemical interaction of the amphiphilic compatibilizer PP-g-MA with the functional groups immobilized on the surface of mullite nanofibers resulted in an optimal filler dispersion.27

The $^{13}$C CP MAS NMR spectra of PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF measured at room temperature are presented in Figure 2. As observed in Figure 2a, the unaged PP sample (u-PP) exhibited three broad symmetrical resonance lines with chemical shifts of 44.14, 26.34, and 21.70 ppm corresponding to CH$_2$, CH, and CH$_3$ carbons.34–36 In addition, a shoulder peak was observed for CH$_3$ carbon at 22.84 ppm related to the most mobile CH$_3$ groups in the amorphous region.36 After UV aging (a-PP), no significant change was observed in the resonance signals of CH and CH$_3$ carbons, whereas the chemical shift at 44.14 ppm for CH$_2$ carbon changed to a doublet, though it was not well resolved. The new peaks at 44.44 and 43.83 ppm indicated the CH$_2$ groups in the crystalline and amorphous regions, respectively.36 Compared to u-PP, unaged PP/PP-g-MA and PP/PP-g-MA/AMNF (u-PP/PP-g-MA and u-PP/PP-g-MA/AMNF, respectively) exhibited slight changes in the chemical shifts of carbon resonances, especially for CH$_2$ and CH carbons. The chemical shifts of CH$_2$, CH, and CH$_3$ were observed at 44.05, 26.28, and 21.28 ppm, respectively, for the u-PP/PP-g-MA sample, whereas these chemical shifts appeared at 44.15, 26.28, and 21.71 ppm, respectively, for u-PP/PP-g-MA/AMNF. The shoulder peak of the CH$_3$ carbon was observed at 22.75 ppm for both samples. The splitting of CH$_2$ carbon into two resonances at 44.52 and 43.87 ppm was well distinguishable in the UV-aged PP/PP-g-MA and PP/PP-g-MA/AMNF (a-PP/PP-g-MA and a-PP/PP-g-MA/AMNF, respectively) samples (Figure 2b,c). Overall, though only slight changes in the macromolecular chain structure of the materials were observed after UV aging from the NMR analysis, the analysis of the structural and molecular damage to the materials associated with UV aging was needed further.

Figure 3 presents the Fourier transform infrared (FTIR) spectra of unaged and UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF samples. For the u-PP sample, the presence of FTIR characteristic bands at 2957, 2916, 2870, 2837, and 2720 cm$^{-1}$ could be assigned to asymmetric CH$_3$ stretching, symmetric CH$_2$ stretching, symmetric CH$_3$ stretching, asymmetric CH$_2$ stretching, C–H bending and CH$_2$ stretching, asymmetric CH$_3$ bending, symmetric CH$_3$ bending, tertiary methyl skeleton deformation, and stretching-induced perpendicular absorption, respectively.37–39 Owing to photooxidation and thermal oxidation reactions on the PP surface upon continuous UV aging, the appearance of carbonyl band at 1850–1650 cm$^{-1}$ was observed for 700 h UV-aged PP sample.40–47 The carbonyl band comprises γ-lactones, peresters, esters, conjugated ketones, aldehyde, and carboxylic acids as oxidation products evolved due to the reaction of the generated macromolecular radicals and oxygen under continuous UV aging conditions.42,43 In addition, the intensity of the PP bands was observed to decrease after UV aging due to the effect of macromolecular degradation. It should also be noted that 700 h of UV aging leads to a significant reduction in the intensity of the bands associated with other oxidation products (except carbonyl groups) probably due to the tendency to decompose41 and/or leach under the influence of water.48 In an earlier study, for 400 h of UV aging, the PP-aged samples exhibited hydroxyl, alkyne, carbonyl, vinyl, and C–O–C bands at 3660–3200, 2150–2025, 1850–1650, 1650–1560, and 1085–1055 cm$^{-1}$, respectively, which almost disappeared after 700 h aging.49 Similar behavior was also observed for the PP/
The u-PP sample exhibited carbonyl band in the aged samples can be solely attributed to PP-carbonyl band associated with the maleic anhydride moiety in MA and u-PP samples, as shown in Figure 4. Further evidenced using the carbonyl index of the unaged and aged samples, as shown in Figure 5.

Figure 3. FTIR spectra of unaged and UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF.

PP-g-MA and PP/PP-g-MA/AMNF samples. The u-PP/PP-g-MA and u-PP/PP-g-MA/AMNF samples did not exhibit the carbonyl band associated with the maleic anhydride moiety in PP-g-MA owing to its low fraction; thus, the appearance of the carbonyl band in the aged samples can be solely attributed to UV aging. The aging effect and carbonyl band generation were further evidenced using the carbonyl index of the unaged and aged samples, as shown in Figure 4.

Figure 4. Carbonyl index of unaged and UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF.

Figure 5 demonstrates the wide-angle X-ray diffraction (WAXD) patterns of the samples. The u-PP sample exhibited characteristic peaks corresponding to the (110), (040), (130), (111), (131 + 041), (160), and (220) α-crystalline planes as well as the (007) γ-crystalline plane at 14.55, 17.26, 19.03, 21.47, 22.18, 25.76, 29.01, and 20.41°, respectively. The related interplanar distance (d) was estimated by applying Bragg’s relation, d = λ/(2sin θmax), where λ (X-ray wavelength) = 1.5406 Å. As a result, the respective d values of 6.08, 5.13, 4.66, 4.14, 4.00, 3.46, 3.08, and 4.35 Å were obtained. For a-PP, the peak diffraction positions did not exhibit any change, though the intensity of the characteristic peaks displayed an increasing trend qualitatively, probably due to the chemocrystallization effect. It indicated the tendency of the amorphous part to undergo degradation initially, followed by the reorientation of the macromolecular structure and, thus, enhancement in crystallinity. In addition, a shoulder peak around 16° also appeared in the aged sample. For u-PP/PP-g-MA and u-PP/PP-g-MA/AMNF samples, the diffraction peaks attributed to PP appeared at slightly lower angles, indicating a slight change in the crystal structure on incorporation of PP-g-MA and AMNF. After aging, the diffraction peaks were observed to shift to higher angles, with the peak positions matching with that of a-PP. In u-PP/PP-g-MA/AMNF, the characteristic (110) peak of AMNF around 16.1° was also observed; however, the peak diminished to a shoulder band after 700 h aging duration. Also, the a-PP/PP-g-MA sample indicated a qualitative increase in the intensity of the diffraction peaks; however, no such increment was observed in the case of a-PP/PP-g-MA/AMNF. Even though the a-PP and a-PP/PP-g-MA samples indicated an increase in the overall crystallinity, further quantification was needed so as to accurately associate this effect with any structural change. As summarized in Table 1 and Figure 6, Xc.

Table 1. Crystallinity of the Unaged and UV-Aged Samples Measured from X-ray Diffraction

| sample                  | Xc (%) | ΔXc (%) |
|-------------------------|--------|---------|
| u-PP                    | 45.7   |         |
| a-PP                    | 56.1   | 10.4    |
| u-PP/PP-g-MA            | 52.6   |         |
| a-PP/PP-g-MA            | 56.6   | 4.0     |
| u-PP/PP-g-MA/AMNF       | 56.2   |         |
| a-PP/PP-g-MA/AMNF       | 56.7   | 0.5     |

\[ X_c = \left( \frac{A_{CRY}}{A_{CRY+AMO}} \right) \times 100 \]

from X-ray diffraction data was quantified using the equation, where \( A_{CRY} \) is the area of crystalline peaks and \( A_{CRY+AMO} \) is the area of all peaks (crystalline and amorphous peaks). The quantified \( X_c \) values were observed to be slightly higher than the differential scanning calorimetry (DSC) measured \( X_c \) values, yet the \( X_c \) variation trend from u-PP to u-PP/PP-g-MA and u-PP/PP-g-MA/AMNF as well as from unaged to aged samples was comparable.

The analysis of UV aging-induced changes in the micro-morphology of the impact-fractured surface of the samples was performed using scanning electron microscopy (SEM), as demonstrated in Figure 7. The fracture morphology of PP indicated an enhancement in the brittle nature with UV aging. The observed structural embrittlement can be expected to result from the photooxidation-induced macromolecular degradation during UV aging. Due to increased structural
embrittlement and the corresponding impact load dissipation inability, the impact strength of the UV-aged sample is expected to diminish. Similar to a-PP, the a-PP/PP-g-MA sample also exhibited a brittle fracture, though the extent of brittleness was much reduced compared to PP, owing to the matrix plasticization by PP-g-MA. Similarly, the extent of brittleness in the a-PP/PP-g-MA/AMNF composite was also observed to be qualitatively smaller compared to a-PP, thus exhibiting a more optimal response to the aging conditions. The surface morphology of the UV-aged samples was also analyzed through optical analysis, as shown in Figure 8. UV aging-induced surface degradation was observed as surface cracks in the samples. Specifically, the appearance of a transverse crack network was noted on the UV-aged surface of the samples, with different characteristics depending on the type of the sample. For PP, a large number of closely located deep transverse cracks were observed after aging, whereas the a-PP/PP-g-MA blend exhibited both small and large (wide and deep as PP) cracks. On the other hand, the a-PP/PP-g-MA/AMNF composite exhibited a small number of wide cracks with large intercrack distance. In addition, the cracks in the composite sample were relatively shallower compared to the cracks observed for a-PP and a-PP/PP-g-MA. As the appearance of the surface cracks during continuous UV aging is related to shrinkage and associated dimensional change, the composite was noted to be the least affected by such phenomena. The observed findings also confirmed the SEM observations about the ability of the composite to effectively withstand the aging conditions.

**Figure 6.** X-ray diffraction measured (a) percentage crystallinity of unaged and UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF and (b) percentage crystallinity increase for UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF.

**Figure 7.** SEM images of the impact-fractured surface of unaged (a1) PP, (b1) PP/PP-g-MA, and (c1) PP/PP-g-MA/AMNF and 700 h UV-aged (a2) PP, (b2) PP/PP-g-MA, and (c2) PP/PP-g-MA/AMNF.

**Figure 8.** Optical microscope images of (a) u-PP, (b) a-PP, (c) u-PP/PP-g-MA, (d) a-PP/PP-g-MA, (e) u-PP/PP-g-MA/AMNF, and (f) a-PP/PP-g-MA/AMNF.

The calorimetric properties of the samples are presented in Table 2, and the second heating and cooling traces of the
samples are plotted in Figure 9. The $T_m$ values of 168.5, 166.1, and 166.4 °C were observed for unaged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF, respectively. Due to the detrimental effect of UV aging leading to macromolecular degradation and molecular weight reduction, the $T_m$ values of the samples were reduced.\textsuperscript{55−60} Specifically, a $T_m$ drop of 13.8 °C was observed for PP after 700 h UV aging, whereas $\alpha$-PP/PP-g-MA and $\alpha$-PP/PP-g-MA/AMNF exhibited bimodal thermograms. The $T_c$ values of 127.9, 127.6, and 127.7 °C were observed for unaged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF, which were reduced by 4.5, 6.7/2.7, and 5.9/2.6 °C, respectively, after aging. The observed drop in $T_c$ of the samples indicated enhanced degree of chemical deformities.\textsuperscript{48,61} Regardless of the sample, $\Delta H_f$ was observed to increase with UV aging in varying degrees, thus indicating a corresponding increase in $X_c$, which also confirmed the findings from X-ray diffraction. The following equation\textsuperscript{50,62} was used for the estimation of $X_c$ for the samples

$$X_c = \frac{\Delta H}{\Delta H_0} \times 100$$

where $\Delta H$ and $\Delta H_0$ correspond to the theoretical $\Delta H_f$ of 100% crystalline PP (207.1 J g$^{-1}$)\textsuperscript{50} and DSC measured $\Delta H_f$ of the samples (normalized to polymer weight fraction). The $X_c$ values of 43.8, 49.9, and 53.7% were calculated for unaged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF, respectively (Figure 10a). It indicated that the addition of PP-g-MA did not result in the reduction of PP crystallinity. Also, the significantly high $X_c$ value in the case of composite signaled the nucleation effect of the filler. After continuous UV aging, the $X_c$ values of PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF increased by 9.7, 3.1, and 0.3%, respectively (Figure 10b), further confirming the X-ray observation of an insignificant effect on crystallinity in the case of $\alpha$-PP/PP-g-MA/AMNF (0.5%). An increase in $X_c$ is opined to be the effect of chemocrystallization, which leads to

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|sample | $T_c$ (°C) | $\Delta T_c$ (°C) | $\Delta H_c$ (J g$^{-1}$) | $T_m$ (°C) | $\Delta T_m$ (°C) | $\Delta H_f$ (J g$^{-1}$) | $X_c$ (%) | $\Delta X_c$ (%) |
|-------|------------|------------------|---------------------------|------------|------------------|---------------------------|----------|------------------|
|u-PP   | 127.9      |                  |                           |            |                  |                           |          |                  |
|a-PP   |            | −4.5             | 98.7                      | 168.5      | −13.8            | 110.9                     | 53.5     | 9.7              |
|u-PP/PP-g-MA | 127.6      |                  |                           |            |                  |                           |          |                  |
|a-PP/PP-g-MA | 120.9, 124.9 | −6.7, −2.7       | 97.4                      | 150.2, 166.0 | −15.9, −0.1     | 98.7                      | 53.0     | 3.1              |
|u-PP/PP-g-MA/AMNF | 127.7      |                  |                           |            |                  |                           |          |                  |
|a-PP/PP-g-MA/AMNF | 121.8, 125.1 | −5.9, −2.6       | 92.5                      | 148.3, 165.8 | −18.1, −0.6     | 95.0                      | 54.0     | 0.3              |
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$T_c$: crystallization temperature; $\Delta T_c$: crystallization temperature variation; $\Delta H_c$: crystallization enthalpy; $T_m$: melting temperature; $\Delta T_m$: melting temperature variation; $\Delta H_f$: melting enthalpy; $X_c$: percentage crystallinity; $\Delta X_c$: percentage crystallinity variation.

Figure 9. DSC heating (a) and cooling (b) traces of unaged and UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF.

Figure 10. DSC measured (a) percentage crystallinity of unaged and UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF and (b) percentage crystallinity increase for UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF.

In accordance with such changes, the cracks appear on the sample surface due to shrinkage and

the reorganization of the degraded noncrystalline sections into crystallites.\textsuperscript{55,54,59,63}
associated dimensional changes. Thus, insignificant crystallinity change in the composite after UV aging is attributed to the observed lower degree of surface cracks, thereby indicating a relatively higher extent of stability toward macromolecular degradation in the presence of filler compared to other materials. Table 3 also details the thermal degradation analysis of the samples, and the thermogravimetric analysis (TGA) thermograms are plotted in Figure 11. The materials exhibited a single degradation step, which remained unaltered after UV aging. Before aging, the composite exhibited marginally better performance than other materials. After aging, the degradation temperatures of the materials were observed to reduce, with PP exhibiting the maximum reduction. Both blend and composite samples exhibited superior thermal stability than the pure polymer after aging. For instance, $T_{50\%}$ and $T_{90\%}$ of the composite were observed to be 436.2 and 465.9 °C, compared to 423.1 and 453.8 °C for a-PP, respectively. These findings also correlated well with the corresponding change in the crystallinity owing to the macromolecular degradation, as observed in DSC and X-ray diffraction.

Table 3. TGA Data of Unaged and UV-Aged Samples

| sample          | $T_{10\%}$ (°C) | $\Delta T_{10\%}$ (°C) | $T_{50\%}$ (°C) | $\Delta T_{50\%}$ (°C) | $T_{90\%}$ (°C) | $\Delta T_{90\%}$ (°C) |
|-----------------|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| u-PP            | 421.1           | 450.8                  | 465.7           |                        |                 |                        |
| a-PP            | 339.0           | −83.1                  | 423.1           | −27.7                  | 453.8           | −11.9                  |
| u-PP/PP-g-MA    | 418.7           | −450.7                 | 466.2           |                        |                 |                        |
| a-PP/PP-g-MA    | 366.3           | −52.4                  | 436.7           | −14                    | 462.1           | −4.1                   |
| u-PP/PP-g-MA/AMNF| 421.3           | 452.5                  | 470.6           |                        |                 |                        |
| a-PP/PP-g-MA/AMNF| 355.9           | −65.4                  | 436.2           | −16.3                  | 465.9           | −4.7                   |

$^aT_{10\%}$: initial degradation temperature; $\Delta T_{10\%}$: initial degradation temperature variation; $T_{50\%}$: maximum degradation temperature; $\Delta T_{50\%}$: maximum degradation temperature variation; $T_{90\%}$: 90% weight loss temperature; $\Delta T_{90\%}$: 90% weight loss temperature variation.

Table 4. Impact and Tensile Properties of Unaged and UV-Aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF

| sample          | impact strength (kJ m$^{-2}$) | Young’s modulus (MPa) | ultimate tensile strength (MPa) | extension at break (%) |
|-----------------|-------------------------------|-----------------------|-------------------------------|------------------------|
| u-PP            | 7.2 (±0.9)                    | 826 (±26)             | 38 (±2.3)                     | 23 (±1.7)              |
| a-PP            | 2.5 (±0.7)                    | 264 (±21)             | 7 (±0.8)                      | 6 (±0.5)               |
| u-PP/PP-g-MA    | 9.4 (±1.0)                    | 833 (±29)             | 37 (±2.5)                     | 29 (±1.5)              |
| a-PP/PP-g-MA    | 4.6 (±0.9)                    | 289 (±25)             | 10 (±1.0)                     | 6 (±0.3)               |
| u-PP/PP-g-MA/AMNF | 28.3 (±1.1)            | 1081 (±34)           | 34 (±1.8)                     | 16 (±1.0)              |
| a-PP/PP-g-MA/AMNF | 14.9 (±1.0)            | 410 (±23)            | 14 (±0.9)                     | 7 (±0.5)               |

Figure 11. TGA (a) cumulative and (b) differential thermograms of unaged and UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF.

Figure 12. (a) Impact strength of unaged and UV-aged samples; (b) impact strength reduction of UV-aged samples.
of the multiphase structural composition. Here, the AMNF and PP-g-MA phases acted as robust stress absorber and compatibilizer to strengthen the interfacial performance, respectively. Under impact load, the composite thus absorbed a high load and generated microvoids through crazing and/or shear yielding, which provided improved stress propagation resistance.\textsuperscript{65,66} The impact performance of the composite was observed to decrease significantly after 700 h of UV aging (Figure 12). The decrease in the impact strength can be attributed to the structural embrittlement resulting from the macromolecular degradation. Therefore, the weathered materials exhibited diminished capability to dissipate the impact energy.\textsuperscript{55,59,67} Comparing the samples, the pure PP matrix exhibited the highest extent of impact strength reduction (Figure 12b). On the other hand, the composite retained a significant impact strength even after 700 h UV aging, which was more than 2 times higher than u-PP. This indicated that the impact performance of the composite was still appreciable after UV aging, thus exhibiting its durability due to the synergistic combination of the filler and compatibilizer.

The tensile modulus of unaged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF was measured to be 826, 833, and 1081 MPa, respectively (Table 4). It implied that the addition of PP-g-MA did not deteriorate the modulus of PP, whereas the addition of AMNF enhanced it by 30%. Figure 13 shows the percent reduction in the tensile modulus, tensile strength, and elongation at break for aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF.

![Figure 13. Percent reduction in tensile modulus, tensile strength, and elongation at break for aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF.](image)

was also the minimum in the case of PP/PP-g-MA/AMNF (Figure 13). As macromolecular degradation resulting from the significant drop in molecular weight is attributed to the observed loss in elongation,\textsuperscript{58–70} it indicates overall superior performance of the composite even after extreme aging.

3. CONCLUSIONS

The objective of this study was to compare the photodegradation of isotactic PP, PP/PP-g-MA blend, and PP/PP-g-MA/AMNF composite in continuous UV aging conditions. The FTIR spectra of the aged samples indicated the formation of various oxidation products upon UV aging. X-ray diffraction studies also signaled an increase in crystallinity, especially for a-PP and a-PP/PP-g-MA, which was also confirmed by DSC. Insignificant crystallinity change in the composite after UV aging indicated a relatively higher extent of stability toward macromolecular degradation compared to other materials owing to the presence of filler. The micromorphology of the impact-fractured surface of the samples indicated an enhancement in the brittle nature with UV aging, with a-PP/PP-g-MA/AMNF exhibiting the lowest extent of brittleness. Also, the composite exhibited a smaller number of shallow surface cracks compared to PP and PP-g-MA. Peak melting and crystallization temperatures of the materials decreased after UV aging, whereas both blend and composite samples exhibited higher thermal stability than the pure polymer after aging. Due to the combined effect of macromolecular degradation, structural embrittlement, and surface cracks, the mechanical properties such as impact strength, tensile modulus, tensile strength, and extension at break were reduced, with the maximum extent of reduction noted for the pure matrix. Owing to the synergistic combination of the filler and compatibilizer in the composite, it exhibited the least reduction, thus confirming its superior performance and durability against degradation. For instance, the use of AMNF in combination with PP-g-MA leads to its better dispersion in the PP matrix, which results in the slowdown of the photooxidation reaction by absorbing the UV radiation and resultant control over alkyl radical release.

4. EXPERIMENTAL SECTION

4.1. Materials. Aluminum nitrate nonahydrate, aluminum isopropoxide, tetraethoxyorthosilicate (TEOS), aminopropyltriethoxysilane (APTES), PP-g-MA (M<sub>n</sub> ~ 9100 and maleic anhydride grafting % of 8–10), and solvents (ethanol and o-xylene) were procured from Sigma-Aldrich and were used directly without further purification. Isotactic PP (HD915CF) was received from Abu Dhabi Polymers (Borouge), UAE. The synthesis of mullite fibers was performed as per the reported literature.\textsuperscript{14,27} The mullite fibers were amine-functionalized using APTES to achieve AMNF, as reported earlier.\textsuperscript{27}

4.2. Preparation of PP/PP-g-MA Blend and PP/PP-g-MA/AMNF Composite. To prepare the PP/PP-g-MA/AMNF composite, 0.5 g of AMNF (5 wt %) was dispersed in 400 mL of o-xylene using an ultrasonication bath at 30 °C for 1 h. Subsequently, 8.55 g of PP and 0.95 g of PP-g-MA were added to the dispersion. The content of AMNF and PP-g-MA was selected on the basis of the preliminary examination, which was reported in our published work.\textsuperscript{27} The mixture was stirred under reflux for 2 h at 130 °C, and the solvent was evaporated at 80 °C in vacuum. Similar hybrids have been reported to have covalent interactions between the AMNF and PP-g-MA phases.\textsuperscript{27} The hybrid sample was processed using
injection molding (Thermo Scientific) at 190 °C with 400 bar for 10 s. PP and PP/PP-g-MA blend (90:10) were also prepared similarly so as to subject the materials to the same processing conditions as the composite.

4.3. Photooxidation. Artificial photooxidation studies were carried out in a BGD 856 UV-light-accelerated aging cabinet from Biuged Laboratory Instruments (Guangzhou), equipped with four fluorescent UV lamps (UVA-340) oriented horizontally on both sides in accordance with ASTM D 4329. The samples were exposed to accelerated UV conditions for 700 h, which was decided on the basis of the preliminary examination reported in our recent work. Specifically, the accelerated aging cycle was as follows: UV exposure with an irradiance of 0.76 W m⁻² at 50 °C for 8 h, combined water spray and UV exposure for 0.25 h, followed by combined condensation at 50 °C, and UV exposure for 1.75 h. In this cycle, the UV exposure imitates the role of sunlight, condensation imitates rain, and water spray imitates dew. Regarding the physical characteristics of the studied samples, standard dumbbell-shaped specimens (ISO 527) with size 75 mm × 5 mm × 2 mm and span length of 35 mm and rectangular bar-shaped specimens (ISO 180) with size 80 mm × 10 mm × 4 mm, prepared by injection molding at 190 °C with 400 bar for 10 s, were used. Throughout this work, the aged samples of PP, PP/PP-g-MA blend, and PP/PP-g-MA/AMNF composite are named as a-PP, a-PP/PP-g-MA, and a-PP/PP-g-MA/AMNF, respectively, whereas unaged samples are named as u-PP, u-PP/PP-g-MA, and u-PP/PP-g-MA/AMNF respectively.

4.4. Characterization. A Fourier transform infrared (FTIR) spectrometer (BRUKER TENSOR II Series) was used for the structural analysis of unaged and UV-aged PP, PP/PP-g-MA, and PP/PP-g-MA/AMNF samples. The FTIR spectra were generated by collecting 32 scans from the thin sections of the injection-molded samples in transmission mode. A diamond attenuated total reflectance (ATR) crystal was used to obtain the spectra in the 4000–400 cm⁻¹ wavenumber region with a resolution of 4 cm⁻¹. The carbonyl index (A_C/A_A) was calculated to further evidence the aging effects, where A_C is the area of the carbonyl band between 1680 and 1800 cm⁻¹ and A_A is the area of reference band between 2700 and 2750 cm⁻¹. X’Pert PRO Panalytical powder diffractometer was used to study the wide-angle X-ray diffraction (WAXD) of the unaged and UV-aged samples. Thin sections from the injection-molded samples were scanned in the 5–60° 2θ region using Cu Kα irradiation with a wavelength (λ) of 1.5406 Å at 45 kV, 40 mA, and room temperature. A step size of 0.017° s⁻¹ and a step time of 10 s were employed. The solid-state nuclear magnetic resonance (NMR) measurements on the unaged and UV-aged samples were carried out using a Bruker AVANCE 400 (B = 9.4 T) spectrometer operating at a Larmor frequency of 100.65 MHz for ¹³C. The spectra were recorded at room temperature using cylindrical 4 mm (outer diameter) zirconia (ZrO₂) rotors at a spinning speed of 12 kHz.

UV-aging-induced changes in the calorimetric properties (melting temperature and enthalpy (T_m and ΔH_m), crystallization temperature and enthalpy (T_c and ΔH_c), percentage crystallinity (X_c), etc.) were assessed using a differential scanning calorimeter (DSC) from TA Instruments. Sample of weight 3–8 mg was examined in the temperature range of 50–250 °C by applying two heating and cooling cycles, using a dry nitrogen flow of 50 mL min⁻¹. Second heating and cooling cycles were used to record the calorimetric behavior of the samples. Further, the thermal properties of the aged and unaged materials were recorded using a TA Discovery thermogravimetric analyzer (TGA) in a nitrogen medium. The temperature range was 35–700 °C, and a heating rate of 10 °C min⁻¹ was used.

AR 2000 rheometer from TA Instruments was used to measure the rheological performance of the unaged samples as a function of angular frequency. The measurements were performed at 190 °C using a gap opening of 1.6 mm. Strain sweeps were recorded at ω = 1 rad s⁻¹ from 0.1 to 100% strain, and the specimens were observed to be stable up to 10% strain. Frequency sweeps (dynamic testing) were thus recorded at 4% strain from ω = 0.1 to 100 rad s⁻¹.

The tensile properties of the samples before and after aging were measured at room temperature with the aid of a 50 kN load cell universal testing machine (Instron 3345). The crosshead speed used for the analysis was 10 mm min⁻¹. The reported tensile data represent the mean of the values from five dumbbell-shaped specimens with size 75 mm × 5 mm × 2 mm and span length of 35 mm, in accordance with ISO 527. The effect of UV aging on the impact strength of the materials was studied at room temperature using Resil Impactor from Ceast (4 J hammer energy). For the analysis, a hammer speed of 3.64 m s⁻¹ was used. The reported impact strength represents the mean of the values from five un-notched rectangular bar-shaped specimens with size 80 mm × 10 mm × 4 mm, in agreement with ISO 180.

The morphology of the impact-fractured surface of the aged and unaged samples was analyzed in a scanning electron microscope (SEM) (FEI Quanta, FEG250). An accelerating voltage of 10 kV was used for the analysis. Prior to analysis, gold sputter-coated samples were affixed on aluminum stubs with the help of carbon conductive adhesive tape. For the examination of surface changes, the micrographs were also obtained using an Olympus BX51M optical microscope, Japan, operated with an ocular magnification of 10X. The dispersion of AMNF in PP was studied by microtoming ultrathin sections in the range of 30–70 nm using a PowerTome equipped with a diamond knife at −6 °C. The sections were collected on 400 mesh formvar electron microscopy grids (coated with copper) and were subsequently examined in an FEI electron microscope (TECNAI) at 200 kV at room temperature without staining. TEM image processing was performed using Digital-Micrograph software (Gatan).

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