**Degradation Kinetics of Multiwall Carbon Nanotube Reinforced Polypropylene During Environmental Aging**

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**Abstract**

The degradation of isotactic polypropylene (PP) and PP-multi-walled carbon nanotube (PP-MWCNT) during environmental weathering resulted in an increased degree of crystallinity, making the materials brittle, and creating spontaneous surface cracks. The degradation resulted eventual breakdown of wafers and increasing the potential for the release of incorporated nano-fillers. Thermal analysis showed wafer’s thickness and reinforcement with MWCNT had a significant influence on the stability of MWCNT-PP composites. Differential scanning calorimetry indicated MWCNTs acted as nucleation points increasing the crystallization temperatures of PP-MWCNT while reducing the extent of aging. Weathering decreased the melting and the crystallization temperatures of PP up to 20 oC where the reduction was inversely proportional to the thickness of the wafers. The activation energy dependencies obtained using isoconversional kinetics of TGA analysis revealed that the effective thermo-oxidative degradations of PP changed during aging. The activation energy for initial stages of thermal degradation decreased from ~330 kJ mol−1 to ∼100 kJ mol−1 for pristine aged PP, respectively, where the values increased to ~300 kJ/mol at later degradation stages. The results suggest the kinetics of early degradation was altered due to the change in the molecular structure of aged PP matrix and the shifting in the degradation rate limiting step.

**Keywords:** *polypropylene, MWCNT, weathering, activation energy, melting-crystallization points*

1. **Introduction**

There are a limited number of studies on the aging of different nanocomposites, and the potential release of imbedded filler materials due to environmental aging. Polypropylene (PP) was selected for this study since it is a thermoplastic commonly used for a broad range of applications such as automotive parts, food packaging, housing materials and electrical devices. PP is a semi-crystalline general-purpose polymer that is cheap, mechanically robust, with high resistance to water and chemicals [1-4]. Nanomaterials have been widely incorporated into polymers to improve the physicochemical properties or provide multi-functions to pristine polymers. Among nanomaterials, multiwall carbon nanotubes (MWCNTs) have been intensively used as an additive to the plastic to make lighter, stronger materials with higher thermal stability, and water resistance [5-9]. Because single- or multi-walled carbon nanotubes are approximately the same length as polymer chain-segments, the interaction and mobility result in marked increase in physical and mechanical properties.

Although nano-reinforcement improves properties of polymers, the added MWCNTs could be released to the environment as composites age or due to mechanical effects during production, usage phase or at the end of their use. Toxicity of MWCNTs human and animal cells and microorganisms has been reported [10-12]. The interaction of released MWCNTs with organic pollutants in the environment can alter the fate and facilitate the transport of hydrophobic organic water contaminants [13, 14]. A recent study showed that MWCNTs adsorbed hydrophobic organic contaminants, polyaromatic hydrocarbons (PAHs), and increased the concentration of the PAHs in water phase [14]. The stability and degradation nanocomposites by environmental aging (e.g., photooxidation, chemical oxidation, and mechanical abrasion) is need to understand the release of nanomaterials from polymer nanocomposites better. Environmental aging may alter the structural, physical and chemical properties of the nanocomposite, which are associated with the stability and degradation and potential release of nano-additives. Although long-term tests under natural service conditions are represented real conditions, accelerated aging tests are carried out to establish in a conveniently short time relative ranking of chemical stability or physical durability materials. Accelerated aging tests simulate weather conditions including sunny and rainy day following pre-selected cycles. These tests are used to estimate or “predict” potential long-term serviceability of material, to elucidate the chemical reactions involved the consequences of releasing of nanoparticles. The test could show the overall pattern of deterioration and guide the long-term performance of materials in outdoor conditions and help to assess whether aging releases embedded fillers. To the best of our knowledge, only a limited amount work has been done to systematically explore the effect of environmental aging on thermal properties of MWCNT-polymer composites [15, 16]. Multi-laboratory aging study of polyamide and epoxy-MWCNT composites done using standardized weathering simulation equipment showed the release of MWCNT [17]. However, extended UV-irradiation of epoxy-MWCNT-amin composite showed no detectable release of MWCNT [18].

This paper is intended to initiate systematic kinetic studies of the aging of polymer nanocomposites in the understanding of the thermal behavior of these exciting materials as polymer structure changes during environmental weathering. We are reporting the results of a rigorous investigation on the environmental effects using changes in the thermal properties of iPP and PP-MWCNT having different thicknesses before and after aging. The effects of environmental aging on thermal decomposition temperature, the estimated degradation kinetics parameter, activation energy, were investigated. We followed analytical methods used to study degradation of plastics [19]. Differential scanning calorimetry (DSC) tests were used to examine the changes in other thermal behaviors such as melting and crystallization temperatures [20, 21] during the aging process.

**2. Experimental**

*2.1 Preparation of Polymer and Polymer-Nanocomposite Wafers*

 Polypropylene (Isotactic, average MW ~250,000 and average MN ~67,000) purchased from Sigma-Aldrich. Commercial MWCNTs (NANOCYLTM NC7000, average diameter: 9.5 nm; average length: 1.5 μm) were obtained from the Nanocyl SA (Figure S1). Granular PP was mixed with 4% (w/w) MWCNTs in a heating chamber installed with mechanical mixing rods (Haake Rheocord 90, Thermo Electron Corporation, Waltham, MA). The content of MWCNTs (4 %) was determined based on previous studies reporting that a significant improvement of physicochemical and electrical properties of pristine materials was obtained with a weight fraction of nanofillers less than 5 wt.% in different composites [22-24]. The mixture of PP and MWCNT was kept above a melting temperature of isotactic PP (165 oC). While melting PP, the mixture was kept mixing for 30-60 min to achieve uniformly distribute MWCNTs in PP. The mixed materials were transferred to an extruder (Rheomex 102, USA), which was adjusted to control the thickness of polymer sheet roles. The wafers of PP and PP-MWCNT composites with three different thicknesses were prepared using the extruder. The prepared samples were denoted based on the composition of MWCNTs and wafer thickness (Table 1). Scheme 1 (Supplementary Section) shows simplified procedures for the wafer preparation of PP and PP-MWCNT nanocomposite. As seen in Figure 1, MWCNTs were well dispersed in PP-MWCNT nanocomposite. The prepared wafers were used for all aging experiment to investigate changes in their thermal stability and property during or at the end of the aging process.

*2.2 Aging of PP and PP-MWCNT nanocomposite*

 The effect of weather and climate on the properties of PP and PP-MWCNT were studied by using accelerated environmental aging chamber (Suntest XLS+, Atlas Material Testing Technology LLC). Samples of PP and PP-MWCNT composite with a width of 5 cm and a length of 5 cm were placed on a stainless mesh plate. The method used for this study follows ISO-4892-2/2013 method for accelerated aging [17, 25]. The plate was put in the accelerating solar aging system (Figure S2). Experimental conditions for the solar aging of samples are provided in Table 2. A cycle of weathering repeated during total experiment duration (3024 h (18 weeks)). Samples of PP and PP-MWCNT composite were taken at 0, 756, 1512, 2268, and 3024 h and total solar irradiant of each sampling time was recorded and converted to real exposure times using annual solar radiant exposure data in subtropical regions (i.e., Florida, USA (6588 MJ/m2)) [26]. The converted real exposure time during the aging experiment was summarized in Table 3.

*2.3 Characterizing Environmentally Aged PP-MWCNT Composites*

Differential scanning calorimetric (DSC) is a thermal analysis technique used to study thermal behaviors of different materials such as melting and crystallization temperatures, enthalpy of melting and crystallization temperatures. DSC was used for detecting the chemical and morphological changes that accompany aging and degradation. Three to four milligrams of the samples were placed in a platinum subjected to controlled temperature variation. The sample pan and an empty reference pan were positioned in the DSC4 pan (TA, DSC Q2000, New Castle, DA) and heated simultaneously to 200 oC at 10 oC/min. The temperatures of the two pans were monitored and the rate of heat flowing to the samples adjusted to keep the temperatures of the two samples equals. The melting (Tm) and crystallization (Tc) temperatures the pristine, and MWCNT reinforced PP before and after aging. The replicate run of each sample was averaged to calculate heat flow at a given temperature (standard deviation 0.6 mcal/sec/g).

TGA (Pyrus 7, Perkin Elmer Inc.) was used to investigate changes in thermal stability due to MWCNT reinforcement of PP, environmental aging, and wafer thickness. The analytical conditions for TGA and DSC are summarized in Table 4. TGA is based on measuring the temperature dependence of the loss of sample weight due to the formation of volatile products. The initial sample was kept as constant for all sample at 3.090 ± 0.135 mg, to minimize variation in the analysis. The rate of the thermal decomposition of materials depends on the temperature the of the samples and the rate of heating, that is the time the sample spends at a given temperature. Thus, the thermal decomposition kinetics of the TGA data provide parameters such as activation energy, *Ea*, and the reaction order (*k*) [27].

 The optical microscopy was carried out on aged composite surfaces HiRox digital microscope – KH 7700 model. A scanning electron microscope (JSM-6490LV, JEOL) was used to observe MWCNTs used to prepare PP-MWCNT composite samples. A transmission electron microscope (TEM, JEM 2100, JEOL) was used to investigate the morphology of PP-MWCNT composites.

*2.4 Theoretical Analysis*

*2.4.1 Crystallization*

 DSC studies are used to estimate the total crystalline content of polymers and composites based on the heat required to melt the polymer. An understanding of the degree of crystallinity of nanocomposite polymer as they age is important since crystallinity affects physical properties such as permeability, density, and melting point. For pristine and carbon nanotube reinforced polymer degree of crystallization, χ, can be quantified by measuring the heat associated with melting (fusion) of the polymer:

 (1)

Where Δ*Ha*is measured melting enthalpies obtained from the experiment, by integrating the calorimetric signal. *W*f is the weight fraction of MWCNT content and ∆*Hm* is the enthalpy fusion of a perfect crystal of 100% polypropylene (207 J/g,) having infinite size [28-30].

*2.4.2 Thermal Decomposition Iso-conversional Kinetic Method*

 Mass loss data from the thermogravimetric analysis can be calculated into conversion, which is the actual mass of sample decomposed and can be defined as:

where *mo* is the initial mass of the sample and *mt* is the actual sample mass.

In the kinetics of thermal decomposition of MWCNT using TGA, one can assume the rate of decomposition is a function of temperature and conversion:

 (3)

The temperature dependent function *k(T)* in Eq. (3) is the specific rate constant commonly by the Arrhenius equation:

 (4)

is assumed for the temperature dependence of k, where *A* is the “pre-exponential factor,” (1/min), is assumed to be independent of temperature, *E* is the energy of activation (J/mol) and *R* is the gas constant (8.314 J/mol.K).

The conversion function is usually expressed as:

 (5)

where *n* is the order of the reaction.

Therefore, the decomposition kinetics equation is obtained by combining the above three equations:

 (6)

The actual temperature under non-isothermal temperature ramping condition can be

 (7)

Where *β* is the heating rate (K/min) and *To* is the initial temperature (K). From Equation 6 and 7, it can be shown that:

 (8)

The integrated expression of Eq. (8) is obtained as

F( (9)

Using Doyle’s approximation method [31, 32] after integrating Equation (9) and using logarithms, it can be expressed as:

 (10)

The apparent activation energy, *E*, can be estimated based on a slope of a linear plot of versus *1/T* to obtain the activation energy as a function of conversion, [32]. Although the expressions used to evaluate these parameters are valid for fluid systems, not for solid-state reactions, they are useful in the elucidation of mechanism involved in polymer degradation.

**3. Results and Discussion**

3.1*Characterization of pristine PP and PP-MWCNT nanocomposites with TGA and DSC*

Several reports have indicated increased thermal stability in nanotube-polymer composites [6]. Non-isothermal thermogravimetric and differential scanning calorimetric behavior PP and PP-MWCNT composites were studied. TGA and DTG curves for a heating rate of 10 oC/min in air showed single-stage high-temperature degradation with the onset decomposition temperature, Tonset, around 400 oC with the maximum weight loss, Tpeak at 470 ± 2.6 oC and 480 ± 3.2 oC for PP and PP-MWCNT composites, respectively (Figure 2(a) and (b)). The mechanism for increased thermal stability could be due to dispersed nanotubes hindering the flux of degradation products which delay the onset of degradation, or the interaction between MWCNT and macromolecular chains of PP slow the degradation that shifts the Tpeak [33].

The small variations in the TGA result of PP samples could be attributed to manufacturing difference in crystal formation changes according to the heat treatment temperatures and cooling densities of thick wafers in using single screw PP sheet extrusion. The temperature of 50% weight loss (T50) for pure PP wafers, decreased slightly with the increased in thickness of samples (Figure 2 (b)). Polypropylene has a density ranging from 0.855 g/cm3 for the amorphous form to 0.946 g/cm3 full crystalline form, and melting temperature ranging from 130 to 170 oC. The decrease in T50 for the wafers of different thickness may be the result of the slight difference in crystallinity and density of thicker samples. The rapid cooling, when crystallized from melt state in the skin of injection mole could be a potential source of error in measured values. Since the lower pressure was applied to thicker wafers when the wafers came out from the extruder, thick wafers may have low density compared to thin wafers due to micron size air pockets. It suggests the added MWCNTs interacted with polypropylene, resulting in slightly improved thermal stability due to high mechanical and thermal stability of MWCNTs [7, 8, 34].

The melting points of pure and MWCNT filled PP were 163 ± 0.62 oC and 162 ± 0.6 oC, respectively, which shows the difference was statistically insignificant. However, the recrystallization temperature increased for MWCNTs filled PP (Figures 2 (c) and (d)), which suggests that the added MWCNTs act like nucleating agents for polypropylene recrystallization [7]. This result is somewhat different from the effects of single walled carbon nanotube on non-isothermal crystallization of polyethylene, where it showed no significant change [35]. The increased recrystallization temperature of PP-MWCNT mix may restrict sites for polypropylene segment, which inhibited the formation of highly ordered spherulites and affects the mechanism of nucleation and crystal growth [7, 34]. The narrow, symmetrical and uniform crystallization curves suggest that heterogeneous nucleation is the predominant crystallization mechanism.

3.2. *Weathering stress cracking of MWCT-PP composite*

Semi-crystalline polymers, like polypropylene, are essentially two phases systems containing spherulitic clusters of crystals surrounded by a continuum of amorphous substance. During the process of aging, PP and PP-MWCNT composites lose their elasticity, become brittle and crack. The light-water spray cycle resulted in photooxidation and hydrolysis resulting in environmental stress cracking. Oxygen diffusions readily through the amorphous region but are highly limited through the crystalline regions. Thus, most of the aging occurs at the spherulite boundaries and weakens the “glue” that holds the crystalline region together. Figure 3 shows SEM and optical microscopic images of pristine and aged polypropylene wafers of increasing thickness PP01, PP02 and PP03. The time for the formation of cracking and crumbling is inversely proportional to the sample thickness following PP01 > PP02 > PP03. There was craze forming as part of crack initiation and continuing formation and growth of cracks with increasing aging, as the PP wafers became increasingly become brittle.

Although PP-MWCNT composites showed higher resistance to aging cracks, increased exposure resulted in significant changes in the surface structures (Figure 4(a) to 4(d)). Aged samples showed exfoliation, surface holes and cracks were evident. The depth in the surface cracks for sample PP42 increased from 15 m to more than 80 m as the aging time increased from 756 h to 2200 h, respectively (Figure 4(c) and 4(d) inserts). The thickness of the oxidized layer can be seen from the depth of the cracked samples (Figure 4(c) to (d)), which is proportional to the UV-aging time or dose.

Aging changes PP structure at the macromolecular, molecular, and the morphological level and thus induce variations in the chemical and structural properties. These exposed surfaces show cracks propagation that increases with the aging time in the stove and penetrates the layer near the surface. The diffusion of oxygen is considered as significant in accelerated test, especially in rapidly oxidizing polymers. Like most semi-crystalline polymers, PP oxidizes exclusively in the amorphous phase because the crystalline phase is impermeable to oxygen. Due to the presence of methyl group in the tertiary carbon atom of PP monomer backbone, the formation of unstable secondary free radicals possible at oxidative conditions. This reaction is kinetically controlled by the diffusion of O2 and H2O in the polymer. Thus, the degraded layer of the PP is in the order of the ratio of the diffusion coefficient and the pseudo-first order kinetic coefficient of the rate constant, *D/k* [36-38].

*3.3. Effect of Aging on Thermal Stability of PP and PP-MWCNT composites*

The presence of tertiary carbon in the chemical structure of PP results in the degradation and changes structural properties [39-42]. Aging of PP causes structural changes, which are typically chain session and crosslinking. TGA measurements of polymers provide information on the thermal stability, composition, decomposition profiles and their products. The thermal stabilities of pristine and MWCNT filled PP having three different thickness both before and after environmental aging were investigated by TGA measurement. The pyrolysis kinetics studies of were conducted based on weight loss versus temperature the sample was heated at the rate of 10 oC/min. Thermogravimetric curves for pristine, PP01, PP02, and PP03 and MWCNT loaded, PP41, PP42 and PP43 samples (Figure 5(a) to 5(f)), respectively. PP degrades by a single mechanism for all pristine and aged samples, which suggests involving the similar rate-controlling step. However, the TGA curves indicate the aged samples exhibited a significant reduction in thermal stability with increased in exposure time. The temperature at 50% weight loss, T50, decreased with an increase in a weathering duration from 470 oC ± oC to around 437 oC ± oC. The thinnest wafers, PP01, crumbled after 1512 h of aging, which was equivalent to an outdoor exposure of 6.9 months in Florida, U.S.A, showing a remarkable decrease in T50 from 470 oC to 434 oC within a short exposure time (Figure 5 (a)). The PP thermal stability is affected by factors such as the presence of additives substances, changes in crosslinking due to aging and the presence of aromatic rings and decomposing functional groups.

DTG data of these samples show the decrease in the Tpeak as the aging time increased (Supplemental Figure S3). PP01 samples were broken into smaller pieces after 1512 h, and they were removed from the weathering chamber and the study. PP02 wafers having thickness 0.39 ± 0.02 mm, were fragmented after 2268 h, whereas PP03 (0.69 ± 0.04 mm) remained intact during the remaining test period of 3024 h. Surface crack formations have been associated with the contraction of the surface layer and the formation of chemi-crystallization [43]. As the intensity of cracking increased with longer aging the materials becomes more fragile. These results showed the effects of photooxidation originate on the exposed surface and diffuse into the inner matrix, thus strength of the sample during aging depended on sample thickness. TGA studies were conducted to monitor the decrease in T50, of PP-MWCNT composite specimens after weathering for selected time lengths. TGA curves for both pristine and PP-MWCNT composites exhibited a one-step decomposition, although the DTG curves for aged samples were increasingly wider with increased aging time. The TGA data for the three samples of increasing thickness initial and aged the PP-MWCNT composite are shown in Figures 5(d), 5(e) and 5(f). The thickest PP-MWCNT composites demonstrated the highest thermal stability with a T50 value of 464 oC after 3024 h weathering. Previous studies reported thermal stability of aged polymer samples decreased due to a combination of photolysis, photooxidation, and thermal degradation of samples [44-46]. Moreover, due to the MWCNT reinforcement, all PP-MWCNT composite samples displayed little structural break down during the full weathering period of 3024 h that is equivalent to 13.9 months of outdoor weathering.

TGA data shows a slight drop in sample weights at temperatures below 250 oC for aged PP wafers that may account for the loss of absorbed water, which promotes further degradation and impacted the dimensional stability of the wafers (Figure 5(a), 5(b) and 5(c)). Previous studies have revealed that absorbed water may exist in a polymer as free water or loosely bound water. Bound water can escape out polymer easily upon heating, and tightly bound water, which is strongly confined in the polymer network and requires additional energy for removal from the polymer [47]. PP-MWCNT composites showed little or no absorption of moisture even after 3024 h of aging. Decomposition of PP due to weathering was caused due to thermal, oxidative and hydrolytic reactions.

*3.4. Environmental aging and changes in melting point*

Differential scanning calorimetry (DSC) allows analysis of thermal effects and monitoring the effects of environmental aging on various phenomena, including melting, crystallization, polymorphism, or specific heat. DSC analysis was done to monitor changes in melting and crystallization temperatures of PP and PP-MWCNT samples that were kept in the accelerated weathering chamber for selected times. The data presented in Figure 6 and 7 show changes in melting and crystallization temperatures of aged samples before and after aging for pristine PP and PP-MWCNT composites, respectively. The critical phase change data are summarized in Table 5.

Melting point depression of PP and PP-MWCNT were observed due to molecular chain scission and formation of carbonyl and hydroperoxide groups. The results of DSC analysis in Figure 6 (a)-(c) showing the melting point, Tm, depression from 162.9 to 142.5 oC for PP01 after 1512 h of accelerated aging, and from 163.8 to 140.0 oC for PP02 after 2268 hr. The drop in Tm for PP03 after 3024 h was from 164.1 to 144.3 oC. Due to structural changes of aged samples by chain scission and oxidation, more aged samples began to melt at lower temperatures, resulting in broadened temperature of melting of samples. A similar trend of a decrease of melting temperatures and extended temperature ranges of melting was observed for aged PP-MWCNT composites (Figure 7(a)-(c)). However, the changes in melting temperatures were not as significant as the pristine PP. The measured Tm values for all initial and after different environmental aging times are shown in Figure 7(d). The changes in the melting and crystallization temperatures reflect the reduction in molecular weight and changes in the degree of crystallinity of polymer matrix that is caused by photolysis, photooxidation, and thermal degradation during weathering. These effects are more significant for thin samples of pristine PP than PP-MWCNT. Figures 7 (b), (d) and (e) show smaller changes in melting and crystallization temperatures of PP-MWCNTs composites than aged-pristine PP. However, all samples show a broadening of melting that increased with aging. The largest change observed was 12.1 oC for PP41 and the smallest changes observed was 2.4 oC for PP43 while melting temperatures of PP01 decreased over 20 oC after 1512 h of aging. These results indicate that added MWCNTs significantly increase the thermal stability of PP. The difference of both melting and crystallization temperatures before and after weathering of PP-MWCNT composites diminished with the increase in wafer thickness. Both Tm and Tc of all aged PP-MWCNTs were higher than aged pristine PP, indicating MWCNTs significantly improved the thermal stability of polypropylene.

Brzozowska-stanuch et al. [44] studied thermal property changes of polypropylene containing different materials (i.e., montmorillonite, compatibilizer, MWCNTs, and blue pigment) by UV aging following the standard method by Society of Automotive Engineers (SAE J2527). They reported melting, and crystallization temperatures of aged polypropylene composites decreased due to structural changes such as polymer chains shortening in the aged samples and found minimal changes in thermal stability of samples containing MWCNTs by UV [44]. The decrease of two temperatures lessened when a thickness of samples increased, which signified the decomposition of polymers by weathering started on the surface of polymers. In particular, changes of both melting and crystallization temperatures of the PP43 sample are very small, only 2 oC decrease, implying that MWCNTs reinforced thermal property of polypropylene and polymer decomposition by weathering occurs at polymer’s surface and then inside of the polymers gradually was degraded [47, 48].

*3.5. Environmental aging and recrystallization*

The estimated degree of crystallinity of aged samples increased by weathering (Figure 6 (d)) and thicker samples were slowly crystallized than thinner samples. Previous studies [49-51] reported similar results that showed an increase in crystallinity of polymer samples after aging, which could be the reduction of amorphous fraction and rearrangement of crystals induced by chain scission and changes of molecular size during the aging process. However, due to the complexity of changes in structural and chemical properties of polymers during aging processes, the crystallinity may increase or decrease [52].

 In addition to investigating thermal properties of aged PP and PP-MWCNT composites, a simple DSC analysis was performed evaluate the aging of the polymer along its depth from the irradiation exposed The thickest sample, PP43, was chosen because three different parts (i.e., top (exposed surface toward solar light), middle (inside), and bottom (unexposed surface)) were taken from this sample only due to its thickness of about 2 mm. As seen Figure 7 (a), melting temperatures of different parts varied with a difference of 2 oC at time 0 and degree of crystallinity of each part was about 4.6% for the top part, 6.0% for the middle part, and 3.7% for the bottom part. As the aging advance, the degree of crystallinity of top and bottom parts PP gradually increased. Samples were taken from the surface of irradiated coupons after selected aging times exhibited increasing degree of crystallinity. However, the changes in crystallinity were less significant for the unexposed side of the coupon (Figure 7(d)). These changes in crystallinity imply that photolysis and photooxidation mainly occur at the surface of samples exposed to solar light and accumulated heat triggers thermal degradation of samples from the surface to the inside, resulting in the decomposition of inside of samples by a long term aging process.

The DSC data on the effects of aging on the melting and recrystallization temperatures of unfilled PP and PP-MWCNT composite are summarized in Figures 8(a) and 8(b). The melting temperature depression was measured by the rate of ~1 oC for every 75 h (for PP01) to 110 h (PP03) of exposure depending on the panel thickness. For PP-MWCNT 1 oC decrease in melting point was measured ranging from every 150 oC for the thin wafers (PP41) to every 320 oC for PP43 (Figure 8(a)). DSC measures showed the recrystallization temperatures were more than 10 oC higher for the PP-MWCNT composite and were not affected by aging, although the decree of crystallinity increased (Figures 8(b) and 8(d)). The decrease in stability of polymer is shown based on the declining T50 with aging time, which indicate changes in polymer molecular structures (Figure 8(c)). The slope of this decline depends on the thickness of the sample and composition that shows the photooxidation of polymers is primarily a surface phenomenon.

*3.6. Thermogravimetric analysis of aged polypropylene-MWCNT*

 This study included estimating the change in one of kinetic parameters, the activation energy, *Ea*, for pristine and aged PP and PP-MWCNT composites. The activation is the most important kinetic parameter, which can be used to predict material storage and operating life [53]. Isoconversional kinetics is an easy-to-use method for kinetics evaluation and is capable of good approximation of complex experimental data. The rate of thermal degradation can be parametrized regarding the extent of conversion as a function of temperature. However, the method is not linked directly to the particular species or reaction molecules of the aged composites. The method typically reflects the overall transformation of the various reactants to products.

We calculated the activation energy, *Ea*, for values varying from 0.05 to 0.95 at a step of 0.05. The values of *Ea* evaluated using the isoconversion method allow a meaningful mechanism and analysis of decomposition kinetics. For the estimation of activation energy, TGA analysis of all samples was conducted by at selected heating rates of 10, 20, 40, or 50 oC min-1. From the set of data of these different heating rates, the isoconversional lines for predefined conversion were calculated, based on Equation 10, section 2.4. The linear plots of versus 1/T for aged samples of PP and PP-MWCNT composites with different conversion values, α, to estimate thermal decomposition kinetic parameter, *Ea*, were calculated from slopes of the linear plots in Figures S5-S10. The estimated effective activation energy values are shown in Figures 9 (a)-(f). At α=0.1, the activation energy for pristine PP01, PP02 and PP03 was 338, 338, and 346 KJ mol-1, respectively. PP-MWCNT composites had a higher activation energy, which was 380 KJ mol-1, 280 KJ mol-1 and 350 KJ mol-1 for PP41, PP2, and PP43, respectively, which confirms increased in thermal stability. It is evident the activation energies after aging decreased significantly with longer aging time. The activation energies for thermal decomposition for material loss from 10% to 50% conversion were significantly lower, which reveals that dominant kinetic process is changing. These results are similar to the values reported in the literature [54]. The activation energy of aged PP01, PP02 and PP03 at 50% conversion indicated significant reduction to 156 KJ mol-1, 128 KJ mol-1, 195 KJ mol-1 after exposure from 1500 to 3024 h. The reduction in the activation energy of aged PP-MWCNT composites were lower than pristine material but not as significant as unfilled PP. The value of *Ea* for the pristine PP and PP-MWCNT composite was nearly constant with thermal conversion, . However, for the aged samples, the significant variation in *Ea*indicates the thermally stimulated decomposition processes are kinetically complex. The increased non-linear relationship of *Ea*with conversion as the PP and PP-MWCNT composites age indicted multistep decomposition kinetics. Weathering degrades the molecular structure of the amorphous fraction and disintegrated weak links that fragmented polymer chains and added carbonyls resulting in a decrease of the activation energy. However, varied patterns of the estimated activation energy over weathering times were observed for each sample due to the complexity of changes in structural and chemical properties during polymer degradation [52, 55]. Moreover, the activation energy for thin samples rapidly decreased compared to thicker samples, indicating that polymer degradation startes from the surface of samples and proceeded to the inner matrix of the samples.

**4. Conclusions**

The aging properties of PP and PP-MWCNT were investigated using thermal analysis techniques to discern the effects of wafer thickness and the filling of MWCNT. Environmental aging of PP has a significant influence on changes in T50, melting and crystallization temperatures, the degree of crystallinity, and the thermal decomposition kinetic parameter, activation energy. TGA analysis showed that T50 values decreased significantly for the pristine PP that were weathered, and this decrease had a direct correlation with the square root of aging time (T50 = a + b). Thin PP wafer samples crumbled in the middle of the test period, which confirmed that accelerated aging is controlled by surface reaction mechanism. All tests performed comparing pristine PP with MWCNT-PP composite showed that MWCNT loading increased the thermal stability of PP. Melting and crystallization temperatures decreased with longer weathering times, but the degree of crystallinity increased in all aged samples. There was a remarkable decrease in melting and crystallization temperatures in aged PP samples. For PP01 coupons, a 20 oC dropped in the melting temperature was measured after 1512 h of weathering while a reduction of 12 oC was observed for aged PP41 for 3024 h of aging. The increased in stability is due to the presence of MWCNTs in PP-MWCNT composites. In all samples, the decrease of melting and crystallization temperatures was inversely proportional to a thickness of samples during the aging process, but the crystallinity of samples was independent to sample depths and increased by rearrangement of crystals induced by chain scission and changes of molecular size during the aging process. The activation energy was estimated as one of the kinetic parameters of polymer degradation. At α=0.1, the activation energy of all samples decreased when exposed to solar light for longer times and the decrease was inversely proportional to sample thicknesses. However, due to the complexity of changes in structural and chemical properties of samples by weathering, different patterns of the activation energy of each sample were obtained for each sample by the estimation study due to the complexity polymer degradation. The results of this study show changes in thermal properties of PP and PP-MWCNT composites by accelerated weathering with thermogravimetric and calorimetric analyses, indicating these analytical techniques are useful to study and understand the polymer degradation by aging in the environment when polymers are disposed during or at the end of their use.

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