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Methine initiated polypropylene-based disposable face masks aging validated by micromechanical properties loss of atomic force microscopy

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HIGHLIGHTS

• Methine induced DFM aging is directly observed by AFM.
• The changes in micro-mechanical properties during aging are quantified by AFM.
• The relationship between micro-mechanical behavior and chemical bond is established.
• Competitive formation of unsaturated bonds during aging can be observed.

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ABSTRACT

The contagious coronavirus disease-2019 pandemic has led to an increasing number of disposable face masks (DFMs) abandoned in the environment, when they are exposed to the air condition, the broken of chemical bond induced aging is inevitably occurred which meantime would cause a drastic decrease of the mechanical flexibility. However, the understanding of between chemical bond change related to aging and its micromechanical loss is limited due to the lack of refined techniques. Herein, the atomic force microscopy (AFM) technique was firstly used to observe the aging process induced by methine of the polypropylene-based DFMs. By comparing the micromechanical properties loss, the influences of humidity and light density on the DFM aging were systematically studied in the early 72 h, and it revealed that the increasing scissions number of the easiest attacked methine (C–H) can gradually decrease the micromechanical properties of the polypropylene (PP)-based DFM. Furthermore, the results are also validated by the in- situ FTIR and XPS analysis. This work discloses that an aging process can be initially estimated with the micromechanical changes observed by AFM, which offers fundamental data to manage this important emerging plastic pollution during COVID-19 pandemic.
1. Introduction

At the end of 2019, the outbreak of highly contagious coronavirus disease-2019 attracted global attention. Evidence suggested that the SARS-CoV-2 virus can enter the human body through the nose or mouth at aerosols (Lukiw et al., 2020). Wearing face mask is a feasible way to curb the virus and block its further spread (Sills et al., 2020). However, its extensive use and some people’s bad habits of discard masks have adverse effects on the ecological environment. Among all disposable face masks (DFMs), the masks composed of polypropylene (PP) are the most commonly used ones, and once they are abandoned in the environment, there will be an inevitable aging process occurring. During aging, it can easily release some microfibers, various pollutants, and induce toxicity, thereby bringing out a potential threat after entering the natural environment (Klein et al., 2021; Morgana et al., 2021; Sullivan et al., 2021; Sun et al., 2021; Wu et al., 2022a).

PP aging is associated with or responsible for the progressive accumulation of the ever-increasing breaking of chemical bonds, and further disintegration into fragments. It is generally considered that the aging process starts when the PP is attacked by light, oxygen, or water from its surroundings. The chemical bond in the polymer chain is firstly broken to generate the free radicals, which would further form hydroperoxides groups to participate in the complex scission reactions and autoxidation. The termination of the degradation reaction occurs in the form of inert products. Unlike most unsaturated chromophoric groups containing polymer, PP does not contain any unsaturated double bonds or functional groups for abiotic hydrolysis in their polymer backbone, thus PP cannot initiate the aging directly under the light irradiation (Liu et al., 2020). However, a large percentage of methine (C−H) in the PP chain and a small amount of unavoidable environmental additions are incorporated into the DFM during the synthesis which can allow initiating degradation to some extent (Taghavi et al., 2021). Because the bond energy of tertiary alkyl radical (\((\text{CH}_3)_{2}\text{C}−\): 8.03 kcal/mol) is lower than that of the secondary alkyl radical ((\(\text{CH}_2\))\(_2\text{C}−\): 10.13 kcal/mol), primary alkyl radical (\(\text{CH}−\text{H}:\): 11.83 kcal/mol), and methyl radical (\(\text{CH}_3\): 14.23 kcal/mol)) (Mathur et al., 1994; Wu et al., 2021b), thus the tertiary carbon atoms (C) of C-H bonds in PP polymers are easily attacked and lead to the formation of polymer radicals. It is inevitably seen that the aging process is often accompanied by significant changes in the mechanical properties of DFM when exposed to the natural environment (Wang et al., 2021). Nevertheless, most researches are focused on their emission products and the relative toxicity in the environment rather than explored the connection between chemical structure and its mechanical behavior (Ishida et al., 2020). To deeply reveal the aging mechanism, the mechanical flexibility properties are expected to be further investigated, especially for the DMF in light-irradiated wet-chemical environments, but still challenging, owing to the lack of relative approaches and means with outstanding resolution at atomic scale characterization and the experimental difficulty in the harsh environment during aging (Wang et al., 2021).

Atomic force microscopy (AFM) with a higher resolution is an advanced analytical technique available sensitive to measuring the surface topography, determining structural and chemical heterogeneities of surface species at the nanoscale (Li et al., 2021; Xu et al., 2021). It can detect subtle differences in micromechanical properties and topography during aging which are not captured previously by macro-scale mechanical system measurements of the polymer sample surface (Collinson et al., 2021; Zhang et al., 2022). And also, the related physical characteristic induced by chemical bond changes can be obtained via the AFM test. The photo-induced topography changes can be quantified by roughness (Ra), which is the most intuitive response to the accumulation of chemical bonds that is broken during aging (Li et al., 2019). Moreover, any intermolecular forces such as the hydrogen bond, van der Waals force, or other chemical bond changed, the adhesion and Young’s Modulus (YM) would be influenced (Kwon et al., 2018; Shen et al., 2018). From the adhesion, the details of hydrophobicity of the structure, the degree of fragmentation, and the adsorption capacity of the DFM in the environment can be obtained (Burton and Bhushan, 2005; Xie et al., 2020). Meanwhile, as the inherent stiffness characterization of the materials, YM can be used to infer the dominant role and bonding types of chain scission and crosslinking (Azuri et al., 2015), as well as assess the difficulty of aging masks to be destroyed (Ayad et al., 2002).

In this work, we report the first use of AFM to test the changes in micromechanical properties of aging DFM. Moreover, Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were combined to confirm the changes. In addition, the induced effect of the C=H bond was determined by Density functional theory (DFT) simulation. The present research contributes to the understanding of the correlation between chemical structure and micromechanics behavior on the nano scale, and provides fundamental data to manage this important emerging plastic pollution during COVID-19 pandemic.

2. Experimental section

2.1. Preparation of samples

The masks used in this experiment were DFM, which were purchased from Henan folca (China). After removing nose seals and ear straps, the DFM was placed in a container uncovered. The irradiation density was controlled at 100 mW/cm\(^2\) by a 300 W Xenon lamp (PLS-XSE300, Perfect Light Irradiation Company, Beijing, China), and the humidity was controlled at 40% and 80% by humidifier (Auxx) and dehumidifier (Deye). The control sample was wrapped in an aluminum foil to make it in dry conditions. Similarly, the paralleled irradiation experiment is implemented by separately controlling the light density of 100 and 200 mW/cm\(^2\), and humidity is 30%.

2.2. Characterisation of materials

2.2.1. AFM

Before the AFM measurement, the silicon wafer was immersed in a Piranha solution (H\(_2\)SO\(_4\): H\(_2\)O\(_2\) = 3:1) for 10 min to remove organic contaminants, then rinsed with pure ethanol and ultrahigh purity water (resistivity greater than 18.25 MΩ cm, TOC less than 10 ppb, and bacteria less than 10 CFU/ml), and finally blew dry with high-purity nitrogen. According to the use of cleaned silicon wafers (Ra < 1 nm), the sensitivity deflection and spring constant of the tips were calibrated by the thermal tuning method, which was about 65.67 nm/V and 1.9440 N/m, respectively (Ferreira et al., 2018). YM, adhesion, surface morphology, and Ra of the DFM, were obtained in contact mode measured on an AFM (Bruker, Multimode 8). For imaging details, the SCM-PIT-V2 tip (Bruker) with a tip radius of 25 nm was used with a scan rate of 0.8 Hz and a resolution of 512 × 512 pixels. To minimize the influence of surface curvature, a 5 μm area at the DFM fiber was selected to take the measurements, which represented at least 100 force-distance curves per fiber, and the DFM measurement at given conditions was counted in three different scan areas on a single DFM to ensure reproducibility (Norman et al., 2021). Adhesion forces and the YM values were extracted from the data using Nanoscope analysis 1.8 software.

2.2.2. SEM

Physical damage and structural changes on the DFM surface were examined using the Scan electron microscopy (SEM, EVO-MA15, ZEISS) with 5 kV electron accelerating voltage. The DFM was cut into small squares (0.5 × 0.5 cm) and placed on the carbon tape affixed by the sample holder. Then the DFM samples were coated with a 2 nm layer of gold for SEM imaging and viewed under 1000 magnifications.
2.2.3. FTIR

The structures of the DFMs were analyzed with a Nicolet-560 Fourier transform infrared-red spectrometer (FTIR). The FTIR parameter set to the wavenumber ranges of 4000–400 cm\(^{-1}\) with 20 scans and the differentiation rate of 4 cm\(^{-1}\). The background spectrum was obtained for each DFM. Two measurements were taken for each DFM surface. After the smooth and baseline correction for the FT-IR spectra using Omnic 8.0 software, 2D-COS analysis was performed using 2DIR software (China).

2.2.4. XPS

X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha\(^{+}\)) with a monochromatic K-Alpha\(^{+}\) line of an X-ray source had been conducted to investigate the chemical bonding state and composition of samples.

2.2.5. Contact angle goniometer

A 1.5 µL water drop was placed on the surface of the samples using a syringe mounted on the contact angle goniometer (SL200KBK0, kino, USA), and allowed to equilibrate for 10 s before acquiring a digital image at least 3 drops were applied to each DFM. The contact angle was determined from the digital images using proprietary software.

2.3. AFM data analysis: extraction of the YM and Ra

The Ra values were calculated by Eqs. (1) and (2) (Liu et al., 2019).

\[
\bar{\tau}(N, M) = \frac{1}{N} \sum_{i=1}^{N} \tau(x, y)
\]

(1)

\[
R_a(N, M) = \frac{1}{N} \sum_{i=1}^{N} (\tau(x, y) - \bar{\tau}(N, M))
\]

(2)

Where \(\tau\) is the current height value, \(\bar{\tau}\) is the average of the \(\tau\) values within the given area, and \(N\) is the number of data points within the given area.

The YM value is calculated by the DMT model in the present study (Fig. S1b). In this model, we assumed the spherical indenting in the flat surface of an elastic half-space object (Fig. S1b). It is a safe approximation related to the electron density can be calculated explicitly in three orders of magnitude (Loskill et al., 2014). Therefore, only the identical difference between the tip and the DFM fiber surface is larger than 2

\[\sqrt{R_d^2 + F_{ad}}\]

(3)

\[E_2 = (1 - \nu_i^2)\left[\frac{1}{E_t} - \frac{1 - \nu_t^2}{E_{tip}}\right]\]

(4)

Where \(E_{tip}\) is the force on the tip, \(E^*\) is the reduced modulus, \(R\) is the tip radius, \(d\) is the sample deformation, \(F_{ad}\) is the adhesion, \(E_t\) is YM value, \(\nu_i\) is the Poisson’s ratio, \(\nu_{tip}\) and \(E_{tip}\) are the Poisson’s ratio and the modulus of the tip. The value of \(i\) is taken by default equal to 0.30.

2.4. Statistical information

Statistical analyses were carried out using a non-parametric Kruskal-Wallis test followed by Mann-Whitney test (two-tailed) for comparisons between two different results under different aging conditions. Besides, the histograms of YM were plotted with identical bin sizes for each DFM sample, then the center of the peak, the average of the YM values, were identified by fitting a Gaussian distribution to the histogram (only when tolerance criteria were 100% satisfied in Origin 8). Standard error was determined as the half-width of the Gaussian peak (Dulińska et al., 2006). Additionally, Pearson correlation analysis was done to define the correlation of CI versus light irradiation time, using IBM SPSS 19 for Windows and the p-value less than 0.05 was defined as significant. The average of the DFM fiber size was calculated by Image J.

2.5. DFT calculation

PP of the geometric structure were calculated at the B3LYP/6-31 G* level in Gaussian 09 system (Liao et al., 2012; Zhu et al., 2022). Then the Multifin with the default settings was used to analyze wavefunction (Lu and Chen, 2012). The orbital-weighted (OW) Fukui function related to the electron density can be calculated explicitly in three Eqs. (5)–(7).

\[f_s^+ = q_N - q_{N+1}\]

(5)

\[f_s^- = q_N - q_{N-1}\]

(6)

\[f_0^+ = \frac{f_s^+ + f_s^-}{2}\]

(7)

where \(N\) represents the number of electrons in the current system.

3. Results and discussion

Light and humidity are two essential factors that determine the degree of DFM aging. At present, the aging behavior is quantitatively determined by measuring the micromechanical properties of adhesion and YM of the DFM during the aging procedure at 3 days (Fig. 1a). Accordingly, the images at a high-resolution atomic scale based on time variation and the corresponding Ra are also captured.

3.1. Morphology evolution

The pristine DFM showed relatively smooth and uniform surface and was packed in a loose form (cotton-like) in a refined structure with a lateral size of around 20 µm (Figs. 1c and S2). Height topographical images were quantified as the Ra values. The integrity morphology of fiber declined, and the Ra values increased gradually when the DFMs were continuously treated by light irradiation and humidity erosion for a short period, then these changes became very prominent after 72 h (Figs. 1b, and S3). The changes mainly contain three obvious steps: cracks, fragments, and collapses (Fig. 1g). A common aging process originated from the exposed surface and then diffused steeply into the inner matrix. The DFM also coincides with this preferential surface aging procedure. It should be noted that the aging process influenced by humidity showed a little difference in a short time. As shown in Fig. 1d, the Ra values increase slowly without light irradiation under the humidity of 40% and 80%, and it has a rather small slope of 0.8100 (Pearson correlation analysis \(r = 0.992, p < 0.01\)) and 0.9986 (Pearson correlation analysis \(r = 0.977, p < 0.01\)) respectively. When the PP fiber was exposed to a relatively light density of 100 mW/cm\(^2\) with the humidity of 40% and 80%, the Ra values increase remarkably and showed a minor difference with calculated corresponding slopes of 0.9886 (Pearson correlation analysis \(r = 0.996, p < 0.01\)) and 0.9986 (Pearson correlation analysis \(r = 0.985, p < 0.01\)), respectively. It is revealed that light irradiation significantly accelerates the increase of the Ra values, which is possibly caused by the more complete photo-oxidation of the C\(^{=\text{C}}\)-H bonds of PP (Von Tiedemann et al., 2020). Therefore, we can see that light exacerbates the destruction of the surface topography, resulting in a sharp increase in the corresponding Ra. As the aging time prolongs, the effect of light on the aging of the DFM is more obvious than humidity.

An extension of light irradiation with different time and densities were thus further investigated, which showed that the exposed surfaces manifested crack propagation and penetrated the internal structure (Figs. 1e, and S4). When the relative light was in a higher light density of about 200 mW/cm\(^2\), the destruction degree was drastic, which was
much larger than that of the light density was 100 mW/cm$^2$. The maximum Ra of 72 h-irradiated at 200 mW/cm$^2$ light density was about 192.60 nm, almost 8.01 and 2.09 times than that of the pristine DFM (with Ra = 24.04 nm), and the maximum Ra of 72 h-irradiated at 100 mW/cm$^2$ (with Ra = 92.12 nm), indicating that the higher light density induced an obvious increase. Furthermore, the aging rate also varies a lot in the whole light irradiation period under different light densities (squares fit with $R^2 > 0.7335$, Fig. 1 f). When the fiber was irradiated at 200 mW/cm$^2$, the increased rate constant of Ra was 13.0766 (Pearson correlation analysis $r = 0.995$, $p < 0.01$) which was bigger than the 100 mW/cm$^2$ light density ($k = 5.3076$, Pearson correlation analysis $r = 0.973$, $p < 0.01$). It has been stated the C-H bond is the easiest attacked position in the PP chain. Thus, higher light density induces drastic photo-oxidation of the C-H bonds of PP in the DFM surface, making more C-H bonds transform into the longer bond length functional groups, which exacerbates crack formation and increases the Ra values (Kataho et al., 2015; Otuchi et al., 1998). Meanwhile, the gradual increase of the C-H bonds scission of the PP chain induces the collapse region to gradually become larger, which can be clearly observed at a high resolution of 500 nm (Fig. 1e2 illustrations).

3.2. Micromechanical properties mapping of DFM

3.2.1. Force-displacement response analysis

Normally, the change of Ra could influence the adhesion behavior of the fiber (Rabinovich et al., 2002). In addition, Ra is a key indicator for judging material aging, which can reflect the change in adhesive strength during aging (Zhou et al., 2021). Fig. 2a shows a typical force versus displacement response for the tip approach and withdrawal on a sample at 0 h ($F = \sim 59 \mu N$). The whole process can be described in a-2
processes containing 6 steps, which the first three steps belong to the extend process, and the following are retract process (detail in Text S4). Adhesion force (stage V) is calculated from the law of Hooke’s law \( F = k \Delta x \); where \( k \) is the spring constant of the cantilever and \( \Delta x \) is the maximum deflection of the cantilever (Li et al., 2019). The environmental condition is under 100 mW/cm\(^2\) light density and 40% humidity called in the present article simply as 100 mW/cm\(^2\)-40%, other conditions in this way. The adhesion forces experienced the same trend for four situations about 100 mW/cm\(^2\)-40%, 100 mW/cm\(^2\)-80%, 0 mW/cm\(^2\)-40%, and 0 mW/cm\(^2\)-80%, which was the first increasing and then decreasing trend with the time increasing, as shown in Fig. 2b-e and Fig. S5. In the increasing stage (I), it is speculated that the hydrolysis and oxidation of C-H bonds induce the generation of hydrogen bonds and polar functional groups to increase the intermolecular force, leading to the adhesion forces exhibiting an increase (Han et al., 2020). At the decreasing stage (II), the continuous oxidation and hydrolysis of C-H bonds cause the DFM surface to generate enough oxygen-containing functional groups, becoming the molecular defects and low-molecular-weight layer (Girois et al., 1996; Han et al., 2018; Rabello and White, 1997; Yao et al., 2022), thus leading to the adhesion forces exhibiting an increase (Han et al., 2020). At the decreasing stage (II), the continuous oxidation and hydrolysis of C-H bonds cause the DFM surface to generate enough oxygen-containing functional groups, becoming the molecular defects and low-molecular-weight layer (Girois et al., 1996; Han et al., 2018; Rabello and White, 1997; Yao et al., 2022), thus leading to a gradual decrease in adhesion forces. When the humidity was 40% and 80% with 100 mW/cm\(^2\) light density, the adhesion force values were \( \sim 38 \) and \( \sim 34 \) nN, which was lower than \( \sim 46 \) and \( \sim 40 \) nN with the light density of 0 mW/cm\(^2\). Based on the result, it further validated that adhesion held a lower value when in a higher humidity condition with the same light density, and its decrease was more influenced by light. This may be attributed to that the C-H bond increasingly suffered from the cumulative photo-oxidation and hydrolysis, thus a low-molecular-weight layer and strong bound water hydration interfacial layer would form in the PP structure (Wu et al., 2020; Yao et al., 2022), reducing the stereoregularity of PP molecular chains under light irradiation and higher humidity conditions (Wu et al., 2021).

Different light densities showed little effect on the adhesion property of the DFM at early times. As shown in Fig. 2f, the mean adhesion forces after 12 h-irradiation DFMs were \( \sim 58 \) and \( \sim 59 \) nN at 100 and 200 mW/cm\(^2\) light density, respectively. However, after 72 h-irradiated, the adhesion forces decreased by \( \sim 26 \) nN with 100 mW/cm\(^2\) light density, while the decreased value was more obviously at 200 mW/cm\(^2\) light density, which was decreased by \( \sim 39 \) nN. Such significant decrease was possibly ascribed to the higher light density aggravating the C-H bonds chain-breaking markedly. Similarly, the different dot areas respecting adhesion in the radar map signified the unevenness initiated by light irradiation (Fig. 2g and h). Not all DFMs could be exposed to sunlight, and some regions obtained full sunlight irradiation may display higher aging extent, and the shady regions might keep the virgin or the low-aged forms (Liu et al., 2021; ter Halle et al., 2016).

3.2.2. YM analysis

When a chemical reaction occurs on the polymer, the increase or decrease of the chemical bond number will change its deformation ability, and this can be reflected by the YM (Fiedler-Higgins et al., 2019; Palermo et al., 2016). In polymer, a chemical bond broken causes a shorter chain length, resulting in a smaller YM value (Kang et al., 2018). However, when the crosslinking reaction occurs in the polymer, such as the hydrogenation of unsaturated bond leading to the increase of the number of the chemical bonds, YM values will increase (Von Tiedemann et al., 2020). Thus, the YM of DFM is of great significance reference in the stabilization judgment of fibers and also the formation and extension of fractures.

Micromechanical properties can be obtained by the histogram, from
which the YM value of the pristine DFM distributed bandwidths normally with an average of ~250 MPa ($E_0 = 249 \pm 0.8740$ MPa, squares Gaussian fit with $R^2 = 0.9030$; Fig. 3a). As the aging time increased, YM values became even smaller (Fig. 3b, and Fig. S6), since the double bonds were induced by the C-H bond of the PP break (Zhang et al., 2020). There was a drastic decrease in YM values after 72 h of light irradiation at 100 mW/cm$^2$ light density ($E_{100 \text{mW/cm}^2} = 26.3048 \pm 0.3800$ and $E_{80 \text{mW/cm}^2} = 44.1475 \pm 0.8736$; least-squares Gaussian fit with $R^2 > 0.9338$; Fig. 3b, and Table S2). It is not surprising that YM values are decreased slowly without light irradiation ($E_{0 \text{mW/cm}^2} = 175.3387 \pm 9.9100$ and $E_{0 \text{mW/cm}^2} = 190.7499 \pm 1.8482$ MPa; least-squares Gaussian fit with $R^2 > 0.8673$; Fig. 3b and Table S2). In addition, the Kruskal-Wallis test correlation analysis also shows that without light irradiation YM values have no significant difference (Kruskal-Wallis test $p > 0.9999$) in early 12 h between 40% and 80% humidity (Fig. 3c and Table S3). Noticeably, the YM began to have a significant difference for 80% humidity when the time increased from 24 h (Kruskal-Wallis test $p = 0.0119$), thereafter extremely significant difference began to occur (Kruskal-Wallis test $p < 0.0001$). However, under light irradiation, an extremely significant difference appeared in the first 12 h (Kruskal-Wallis test $p < 0.0001$, Fig. S7). Whereafter, there is no significant difference in YM (Kruskal-Wallis test $p > 0.9999$, Table S3) in the humidity atmosphere even at 72 h. Based on the above observation, we can also obtain that light as the main influencing factor caused the great loss of the micromechanical properties.

To further validate our supposition, principal component analysis (PCA), one of the most widely used methods for data exploration and visualization (Abid et al., 2018), was used to find out and assess the similarities and relationships between humidity and light density. Fig. 3c represented the PCA plot of the YM at three factors of the aging DFMs, which observed variance with light density contributing 41.84%, humidity contributing 31.39%, and time contributing 26.76%. The values of the principal component are calculated by three components and corresponding eigenvectors (Table S4), and it can be concluded that there is a linear relationship between the variable factors and the aging process as shown in Fig. 3d (squares fit with $R^2 = 0.8761$). Thus, the loss of the micromechanical properties of DFMs is more susceptible to light.

By comparing with the pristine DFM (Fig. 3a), it was surprised to find that the changes of the YM were rather different from the previous reports from which the YM normally experienced a steady decline or a first increase then a decreasing trend shown in Fig. 4a (Fajardo Cabrera de Lima et al., 2020; Joseph et al., 2002; Lv et al., 2017). However, in this work, the YM mainly experiences a decrease at the beginning of the light irradiation, then shows a slow increase, and finally performs a dramatic decline. This might be due to the different observation periods and the

![Fig. 3](https://example.com/fig3.png)

**Fig. 3.** The histogram of the YM of a the pristine DFM and b the DFM at different environmental conditions by the gaussian fitting. c PCA biplots. The direction of increase for a given variable is pointed by each vector and its length represents the strength of the correlation between the variable and the ordination scores. d Fitting curve of principal component and YM values of the DFMs at the different aging times.
used apparatus. It should be noted that for most aging processes, the initiation process took place at the very beginning time even for several days, and such subtle only can be detected by a high-resolution apparatus. At present, we select 3 days as a research period to detect the early changes by AFM (Fig. 4a-c and Table S5). We have declared that the broken of C–H bond was responsible for the aging process of DFM, which could also induce the formation of a more flexible chain arrangement (Wu et al., 2020), such as cross-linking, chain fracture, and oxidation in the local polymerization chain. In the initial-decrease period, most of the C–H bonds of PP chain scission induced the structural changes of aged DFMs, leading to YM values gradually dropping in the micromechanical properties. Then a transient ascended was ascribed to the rearrangement of previously stretched amorphous segments, which might produce densifications of amorphous regions of the oriented PP polymer (Dudić et al., 2000; Islam et al., 2010). While the following decrease stage was resulted from the defect formation caused by oxygen-containing functional groups (Figs. 5a and 6a). Moreover, at beginning of 12 h, YM values were 182.0184 ± 6.4936 and 120.5838 ± 6.1850 MPa at the 100 and 200 mW/cm² light density, respectively, indicating that the different light densities induced the mean YM values were the significant difference at the 0.001 level (Kruskal-Wallis test p < 0.0001, Table S5, 6). However, after 48 h, the significant difference decreases (Kruskal-Wallis test p = 0.0612). This phenomenon is related to the fact that the DFM in the environment would not be continuously aging at a constant rate, and it may exist as small-sized fragments (submicron or nano plastics) in the environment for a long time during the entire life period (da Costa et al., 2016).

Based on the results of the micromechanical mapping, we confirmed that light as the main factor, can induce the break of the C–H bond of the PP fiber and initiate the aging process even at a very early period. The detailed processes were described in Fig. 4d. During the whole observation period, YM presented a total downward trend, and it decreased gradually with the accumulation of the dehydrogenation reaction of the C–H bond. It is worth mentioning that the YM values rapidly decrease on account of the scission of the C–H bond and the appearance of oxygen-containing functional groups on the DFM, but there is a convalescent phase due to the rearrangement of the amorphous segments. Accordingly, under the oxidation and hydrolysis of methine (before 36 h), the induced intermolecular forces caused the adhesion to increase firstly as the reaction of the C–H bond continuous, and it reached a saturation situation making the low molecular layer formed and resulting in a decreased adhesion force.

![Fig. 4](image-url)

Fig. 4. a The YM values of the DFMs at different aging times. “NS” represents no significant difference. “*” represents difference at 10% level. “**” represents significant difference at 5% level. “***” represents significant difference at 1% level. Error bars indicate 95% confidence intervals. The histogram of YM of the DFM by the Gaussian fitting at different light densities: b 100 mW/cm² and c 200 mW/cm². d The schematic diagram of the changes in the micromechanical properties of the DFM with the irradiation time.
3.3. Chemical structure of DFM under 200 mW/cm² light irradiation

3.3.1. FTIR analysis

In general, the in-depth analysis of chemical structure changes is conducive to reveal the aging process. At present, we selected the DFM changes under the irradiation with the light density of 200 mW/cm² as the research target and detected it by FTIR (Fig. 5a) and XPS (Fig. 6a). FTIR was used to analyze structural changes of the DFMs after light irradiation (Fig. 5a). The main components of the PP-based DFM are -CH, CH₂, and -CH₃ groups, the vibration peaks located in 2950, 2870, 2918, and 2835 cm⁻¹, respectively. And the easiest attacked C-H groups are located at 997 cm⁻¹(Ranjan and Goel, 2021). The signal of carbonyl (C=O), alkanyl (C=C), and hydroxyl (O-H) region was not discovered in the pristine DFM (Fig. 5a), whereas the peaks would come out at 1715, 1640, and 3400 cm⁻¹ after irradiated, respectively (Semilin et al., 2021), which can be attributed to that the C=O in the PP chain was more easily to be attacked, facilitating the reaction of C=O bond with oxygen and water to form massive of the oxygen-containing functional groups (Yousif et al., 2012). And also the C-H bond can be induced by the additive in the DFM to form the alkanyl group on the surface during aging (Taghavi et al., 2021; Xie et al., 2022). Under this circumstance, the hydrophilicity and polarity would be enhanced, and accordingly, thermal stability (Fig. S8) and the contact angle reduced (Fig. 5c) (Wu et al., 2021b).

To quantitatively determine the C-H conversion to C=O groups during aging, the carbonyl index (CI) was calculated by the ratio of the maximum carbonyl peak at 1715 cm⁻¹ to the reference peak at 974 cm⁻¹(Wu et al., 2021b). At present, the CI of the DFMs shows a trend of initially slow and then fast increasing as a function of light irradiation time (Pearson correlation analysis r = 0.9270, p < 0.01, Fig. 5b), suggesting that the abundance of the C=O groups is suitable for reflecting the changed properties of DFMs, and an induction period is required during the continuous photo-oxidation (Liu et al., 2021). In the induction period (0–24 h), the C-H bonds of PP break and then form polymer radicals caused by the light absorption, followed by the addition of oxygen and water from the surrounding to form hydroperoxides and the generation of oxygen-containing groups on the DFMs (Gewert et al., 2015). Additionally, the competition formation of C=O and C-O groups induced by C-H bonds would also result in lower CI in this period (Liu et al., 2021). It should be noted that the oxygen functional groups are critical to exacerbate the aging process, due to their strong absorption of light (Zhu et al., 2020). After the induction period, the synergistic accumulation of the massive reactive radicals and the oxygen-containing groups exacerbated the aging process, producing a high CI.

To elucidate the dynamic process of photo-induced groups evolution, the time-dependent 2D correlation spectroscopy (2D-COS) -IR was used to investigate the formation sequence of the functional group (Noda et al., 2000; Zheng et al., 2010). Through the 2D-COS infrared full spectrum (Fig. 5d-g), it can be obtained that the band appearance sequence follows the order: 997(CH- → 1163 (C-O) → 1646 (C=C) → 1710 (C=O) → 1375 (CH₃ symmetric deformation) → 1456 (CH₃ asymmetric vibrations or CH₂ scissor vibrations) → 2950 (asymmetric stretching vibrations of CH₃ groups) → 2916 (asymmetric stretching vibrations of CH₂ groups) → 2834 (symmetric stretching vibrations of CH₃ groups) → 2868 (symmetric stretching vibrations of CH₂ groups) cm⁻¹. It is evidently to see that the C-H is the induced group in the whole aging process, and as the C-H bond breaking accompanied the bonding

![Fig. 5.](image-url)
group changes during PP aging. In addition, what needs special attention is the bands at 1712 and 1646 cm\(^{-1}\) in the synchronous 2D-COS spectra and a negative cross-peak in the asynchronous spectra, indicating that the 1646 cm\(^{-1}\) bands appeared earlier than 1712 cm\(^{-1}\). Thus, the newly C=O groups were generated followed by C-O groups during light radiation, which might be caused by additives in the DFM (Gewert et al., 2015).

### 3.3.2. XPS analysis

XPS characterizations further provided insights into the surface functional groups' contents before and after irradiation treatments (Fig. 6a). For the pristine DFM, C 1s spectra show that the samples have a significant C\(_2\)-H and other C-H (C\(^2\)-H) binding component. However, the C-O bond peak is also observed at ca. 286.25 eV, owing to the presence of additives during the synthesis process of the DFMss (Xie et al., 2022), which is also confirmed by the organic elemental analysis (Table S7). After irradiated, the C 1s peak is split into six peaks after light irradiation, located at 285.00, 285.17, 286.25, 286.88, 287.53, and 288.20 eV corresponding to C\(^2\)-H, C\(^2\)-O, C=O, C=C, and O=O=C, respectively (Beaumond and Briggs, 1992; Yao et al., 2022). The relative contents of the C\(^2\)-H bond decreased from 24.77% to 18.24% in the early period (0–24 h), and then gradually decreased to 5.6% after 72 h. It is worth mentioning that the percentage of the C\(^2\)-H bond slowly decreased from 49.65% to 25.36% with time up to 24 h, and then rapidly increased to 51.27% after 36 h, finally, gradually decreased to 26.87%. However, the relative contents of the C=O bond increased to 2.90% with time up to 24 h, and then rapidly increased to 29.53% after 72 h. This result validated the C\(^2\)-H bond broken gradually accumulated during aging, then the C=O bond was preferentially generated may be on account of the fact that the hydrogenation of the C=C bond is thermodynamically and kinetically more favorable than that of the C=O bond, leading to the decrease of the C=C bond (Meemken and Baiker, 2017; Tamura et al., 2017). This indicates that the C=C bond plays a dominant role in the early aging stages (0–24 h), and the C=O bond takes a second role. Besides, a very low-density signal is observed in the O 1 s spectra of the pristine DFM on account of the absorption of molecular water, adsorb oxygen (Yan et al., 2021), and oxidation (Table S8). The corresponding O 1 s peak was fitted by adsorption oxygen (531.33 eV), O-H (531.48 eV), O=C (532.71 eV), H\(_2\)O (532.68 eV), O-C (533.35 eV), and chemical adsorption oxygen (534.64 eV). It can be seen that the relative contents of O=C groups increased to 37.78%. Furthermore, the relative contents of O 1 s increased from 7.29% to 8.43% (Table S8), which also possibly suggested that more oxygenated species generated on the DFMss surface after the light irradiation treatment. Thus, we can see that the reactive formation of the physically adsorbed oxygen and water-reactive contributes to increase the surface hydrophilicity and reduce the micromechanical properties of the DFM during aging.

### 3.4. Discussion on the relationship between chemical structure and micromechanics

At the nano scale, AFM investigation revealed the DFMss’ aging as the surface morphology and roughness significantly changed. Combining our results with CI research, Fig. 6b illustrates a good linear correlation between the CI and the Ra in the apparent topography (Pearson correlation analysis \(r = 0.983, p < 0.01; R^2 = 0.8563\)). These results show the oxygen-containing functional groups that develop on the DFM surfaces, resulting in higher surface roughness due to the generated nano-granular oxidation, pits, and flakes (Fig. 1e2). The rougher surface supplies an enlarged surface area for UV-vis irradiation and oxygen, which further accelerates aging. However, more research efforts are needed to clarify these aging processes.

Furthermore, the orbital-weighted (OW) Fukui function was
calculated to clarify the more easily attacked active sites during photo-
aging of PP. Thus, the relationship between the OW Fukui function and
PP degradation was analyzed, and the OW Fukui index of each atom was
summarized in Table S9 and the corresponding of each atom was
marked in Fig. 6c. The higher index indicated the more easily attacked
active sites which were marked in gray. The higher $f^+$, $f^-$, and $f^0$ value
represent the higher attack tendency for $h^+$, $e^-$, and radicals, respect-
ively. It could be found that the C-H (C-H$_{\text{C}}$) bond was more easily to
be attacked by e$^-$ and radicals, respectively (Fig. 6c and Table S9). As
shown in the 2D-COS analysis (Fig. 5d-g), the aging is initiated by the C-
H bond. Furthermore, the XPS quantitative analysis of the C-H bond
(Fig. 6a) was further validated that the C-H bond was gradually broken
during aging, then the C=C bond was preferentially generated due to
the existence of additives, leading to the formation of oxygen-containing
functional groups (Table S8). This result is consistent with the micro-
mechanical behavior from AFM. In the first stage, the YM decreases due
to the C-H bond cleavage, then even recovers induced by the hydro-
genation reaction of the C=C bond, and finally reduces owing to the
accumulation of carbonyl group (Fig. 6d). These changes in chemical
structure and micromechanical behavior show that AFM measurement is
closely related to the results of conventional chemical analysis.

Based on the above data analysis, we can see that the easily attack-
able C on the PP backbone is responsible for the PP aging (Mathur et al.,
1994), initiating the introduction of the unsaturation bond, and the
detailed aging process is shown in the Scheme 1. When the PP was
exposed to light irradiation, the additives existing in the DFM (Table S7,
10) lead to the cleavage of the C-H bonds in the PP backbone, initiating
a free radical chain reaction and forming alkyl radicals (Gewert et al.,
2015; Taghavi et al., 2021; Xie et al., 2022), then the C=C bond would
be preferential formed (Lazar et al., 2000), which was a dominant re-
aaction at the early period (Pathway 1). The alkoxy radicals subsequently
reacted with the PP backbone and produced hydroperoxide groups
through hydrogen abstraction. Alkoxy radicals were ultimately trans-
formed into oxygen-containing functional groups (e.g. C=O bond)
through $\beta$-scission reaction (Pathway 2) (Wu et al., 2021b). The hy-
drogenation of the C=C bond is thermodynamically and kinetically
more favorable than that of the C=O bond (Meemken and Baiker, 2017;
Tamura et al., 2017), thus the oxygen functional groups will gradually
replace the dominant position of the carbon-carbon double bond with
aging. It should be noted that such transition might come from the
catalytic effect of Cd, Cu, Zn, or other metals existing in the PP-based
DFM (Table S10) (Bussan et al., 2021; Mohr and Oestreich, 2016).

4. Conclusion

Through the AFM test, we directly observed that the broken of the methine (C-H) bond is the initiate step during the PP DFM aging, which is based on the loss of micromechanical properties of DFM. The light effect is more remarkable than humidity during aging of DFM. The adhesion and YM parameters were quantized by the loss of the C-H

\begin{center}
\textbf{Scheme 1.} Possible mechanism of aging of the DFM.
\end{center}
bond. In a 72-h observation period, YM values show the trend of first decreasing, then subtle increasing, and final decreasing, while the adhesion exhibits two steps with a first increase then a decrease step. This observation suggests that the unsaturated carbon-carbon and carbon-oxygen double bonds produced by the breaking of C=H bonds of PP are closely related to micromechanical. These results are consistent with the analysis of the FTIR and the XPS for the aging DFM, from which the C==C bond is preferentially formed in the early, after then, as the scission of the C=H bonds, the C==O bond generates gradually and becomes a dominant functional group. It can be concluded that the micromechanical properties tested by AFM can be used to determine the aging degree of the DFM, and further explore the aging mechanism.

Environmental Implication

The ever-increasing aging disposable face masks (DFMs) would release quantity hazardous pollutants which have posed a serious threat to the ecology. Thus, to accurately determine which group is an initiated group is crucial during DFM aging. Herein, we firstly revealed that the increased number of breaks in the easiest attacked methine group (C==H) reduces micromechanical properties of the DFM and plays a critical role in the DF aging. Furthermore, the observations also contributing to assessing the correlation between chemical structure and micro-mechanics behavior of aging DFM, and the impact of the pollution and the plastic materials.

CRediT authorship contribution statement

Xueqin Chen: Conceptualization, Methodology, Writing – original draft, Investigation, Formal analysis, Validation. Mude Zhu: Supervision, Investigation, Writing – review & editing. Yi Tang: Methodology, Supervision, Writing – review & editing. Huiyuan Xie: Investigation, Writing – review & editing. Xiaoyun Fan: Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.129831.

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