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Mechanical and Thermal Properties of Aged Helmet Outer Shells Made of Acrylonitrile-Butadiene-Styrene

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Abstract: *Acrylonitrile-butadiene-styrene (ABS) material is widely used as a protective rigid shell and impact absorber in bike helmets, providing vital protection against head injuries under specific working conditions. However, ABS aging in helmets could affect the safety factor of helmets and shorten the service life. Exploring the transformation during aging process for real assembled helmets made of ABS out shells is crucial for the investigation and fabrication of high performance helmets. Herein, the effect of long-term aging on the physical properties of practical helmets made of ABS outer shells has been discussed systematically. Four different types of helmets were subjected to different aging conditions, i.e., outdoor environment, ultraviolet exposure, hot air, and humid-heat conditions. The impact property and stiffness tests were carried out as a function of aging time and aging conditions. The measured helmets were capable of meeting engineering tolerances when aged under outdoor, ultraviolet, and hot air conditions, and could deliver competitive mechanical performance to their pristine helmets. Yet, after aging under humid-heat for 800 h, the helmets showed an obvious decrease in impact strength, gloss, and stiffness. The influence of different aging conditions was further investigated by thermal and spectral characterizations. The study might provide some valuable advice for helmet performance evaluation.*

Keywords: *Helmet, ABS resin, Aging, Humid-heat*

1. Introduction

While the cost of gasoline and fuel-driven vehicles has increased sharply, alternative, cost-effective, and green transportation is necessary to enable embracing of sustainable development. Controversial studies have suggested the growth of bikes and electronic bikes, which might ease the everlasting CO_2-releasing and cost-energy-saving issues [1-3]. For those bike riders, the law requires that all should wear helmets without any exceptions. The helmet could provide vital protection against head injuries under specific working conditions [4, 5]. It has become important to develop high performance helmet for workers and the associated product investment system.

The protective helmet usually is comprised of outer shell and polymeric foam inner liner, where the shell part could absorb nearly half of the external impact energy and the liner part could be used as lightweight damping and absorbent element [6-8]. Several works have been reported on the comparsion of different materials as outer shells for the helmet and improving the strength related properties including stress, strain and deformation. The shell materials of helmet can be made of polycarbonate (PC) composites, S-Glass, Carbon Epoxy, Polyethylenen, Nylon4-6, polyether ether ketone, Polyester, and Polyphthalamides [9-11]. Among those choices, PC and acrylonitrile-butadiene-styrene (ABS) are most widely used as PC presented extraordinarily high impact resistance, high tensile strength, and transparency and ABS has a higher impact resistance strength than any other common plastics [12].

When used in helmets, the outer shell materials are exposed to various stimuli including heat, humidity, oxygen, ultraviolet (UV) light, and other factors that can degrade their properties over time.

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Polymer degradation from those factors can decrease the safty of the used helmet and cause fatal injure in accidents. Herein, the performance of the outershell materials throughout a variety of environmental exposures (heat, humidity, ultraviolet, etc.) across its lifetime are essentially important for their application. Although, the ability of ABS has shown excellent performance at exposed conditions (oxidation, degradation, distortion, etc.) [13-15] and their impact-absorbing properties and failure mechanism has been well investigated [16], few studies have focused on the effect age has on the real helmet products. For instance, Pearsall et al studied age effects in 10-year-old hockey helmets [17,18]. Kroeker et al studied the impact attenuation properties of expanded polystyrene foam in used bicycle helmets change with age [19]. Based on these limited data, there is a lack of comprehensive understanding of the exposure factors on the aging behavior of real bike helmets.

Herein, we presented the groundwork for the development of environmental tests to assess the impact resistance performance, thermal properties, and mechanical properties of helmets made of ABS outer shells. This work attempts to systematically compare the properties of different ABS-based helmets under various conditions, with the aim of identifying the long-term usability and criteria for a helmet under practical applications. It would be useful to identify the protective performance of the helmet for worker injury tolerance and the designing of proper helmets. For this purpose, we began setting up the testing about 8 months ago, and four different types of helmets were selected and subjected to regular outdoor environments, ultraviolet exposure, hot air, and humid-heat conditions. The experimental data was compared and the drawn results provide valuable advice towards quantifying energy absorbing capability of a helmet and the risk of usage.

2. Materials and methods

2.1. Materials

All helmets were produced by a local factory as requested, using different outer shell materials: Helmet A (ABS1#:PC = 30:70, GP-5006B, LG Korea), Helmet B (ABS1#, PA-709, Meichi Technology Co., LTD), Helmet C (ABS2#, PA-709 with 10% master batch, Meichi Technology Co., LTD), and Helmet D (ABS3#, DG-417, Tianjin Dagu Chemcial Industry Co., LTD). The helmet samples were produced with an standardized industrial process for B3 half helmets. The helmet shells were produced following the steps of injection molding-edge griding-primer and top coating-varnish. The cushioning layer is black EPS (thickness: 1.4 ± 0.2 cm, density: 15 ± 0.5 kg m^{-3}, Tianjin Stanley New Materials Co., Ltd.), and the comfort pads are all brown leather and suede. The outer shell has a uniform thickness of 2.0 mm. All received helmets were assembled with the same parts and decorating. The head circumferences of helmets were 580-600 mm. The heights from base plane to reference plane were 29 ± 1 mm and the heights from the reference planes to the top of helmet were 107 ± 2 mm. The weight of the finished product is between 540-600 g.

2.2. Aging test

Outdoor aging tests were conducted by simply placing helmets on the roof of the laboratory space for 8 months. The experiments were conducted in Hangzhou, China (30.2741° N, 120.1552° E) where the average test temperature was 17.8°C, humidity 70.3%, and sunhine duration 1765 h. Hot air aging was done by placing the helmets in an air-circulating oven, maintaining the working temperature of 65 ± 2°C and air circulation (DHG-850, Wuxi Silian Technology Co., Ltd.) for 500 h, 800 h, and 1200 h. For UV aging, an accelerated aging test chamber (ZW-735, Qingdao Zhongbang Instrument Co., Ltd.) was applied for helmets, using a 450 W short-wave pulsed xenon lamp (working distance between lamp and the top of helmet: 150 ± 5 mm) for different testing time periods. The testing temperatures were maintained below 60°C. Humid-heat aging tests were accomplished in an oven (DHS-500, Wuxi Silian Technology Co., Ltd.) at 85 ± 2°C and relative humidity 85% for different time periods. The outer shell of the aging helmats were cut into squares (42 mm × 26 cm) for testing.

2.3. Characterization

Impact tests were performed on Drop tower system (HT-6011, Dongguan Hongtu Instrument Co., Ltd.) with a flat surface; Helmets were examined by determining the acceleration on the model steel head (note: targeted impacts of ≥ 150 g). The impact heigh were 1600 mm. Samples were placed at 21 ± 5°C and a relative humidity of 40-80% prior to tests. Three measurements (front midpoint, left midpoint, and right midpoint) were collected on each helmet and the maxium peak acceleration values were reported. Stiffness of helmets was measured with the helmet lateral deformation testing machine (HT-6021, Dongguan Hongtu Instrument Co., Ltd.) following the method provide by GB 811-2010. Heat deflection tester (HV-3000-P3, Gotech testing machines Inc.) was applied to measure VICAT softening temperature and to evaluate the thermal properties of outer shell materials. HDT-CNS testing method was selected, and the measurements were conducted with a heating rate of 120°C min^{-1} at 0.455 MPa. Scanning Electron Microscope (SEM) images of the sample surfaces before and after aging were captured with a ZEISS Sigma 300, equipped with a Sputter Coater (Oxford Quorum SC7620). Fourier-transformed infrared (FTIR) spectra were obtained on a Thermo Scientific Nicolet 5700 Analytical FTIR spectrometer using attenuated total reflection (ATR) mode. Differential scanning calorimetry (DSC) measurements were performed on a NETZSCK DSC 200F3 under a N_2 atmosphere with a ramping rate of 10°C min^{-1} for heating and 5°C min^{-1} for cooling. Dynamic mechanical analysis (DMA) (TA-Q800) was used to measure the storage modulus and loss modulus of samples at a heating rate of 3°C min^{-1} and 1 Hz of frequency. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA 2 analyzer with a heating rate of 10°C min^{-1} under N_2 atmosphere, with a continuous flow of 60 mL min^{-1} and 40 mL min^{-1} through the sample furnace and the balance compartment, respectively.

3. Results and discussions

Whether the helmets can withstand the external impact is an important index of their safety factor. In this paper, we first carry out the an comprehensive study on four groups of helmets with different consistents. In order to evaluate the effect of single aging condition on the impact performance of helmets, we used UV light, hot air flow, and humid-heat to age all helmets respectively, and further investigated their aging behavior.

The appearances of helmets after various aging conditions were presented in Figure 1. All helmets showed similar physical integrity features except the humid-heat aged samples. It is clear that the aged helmets showed significantly poor shiny feature compared with the pristine helmets. After 800 h humid-heat aging process, all helmet samples exhibited deformed shapes with its outer shell and liner detached due to the polymer chains degradation, chains scission, and cross-linking of the polybutadiene. Notably, as shown by the aging testing, the type-A helmet exhibited the smallest changes comparing to the other conterparts. This can be ascribed to the presence of large amounts of PC phase (70%) with they type-A formulation as the PC is known to be more stable than ABS.

Next, a quantitive comparsion was revealed by investigating the impact resistance of the helmets via impact tests. Generally, a standard helmet shows low peak acceleration values within threshold limit value (below 150 g), indicating this standard helmet meets the tolerance criteria for practical applications. We first compared the helmets stored outdoors (exposure to sunlight for 8 months) to the pristine helmet (Figure 2c), and found that the current status exhibited insignificant enhanced impact resistance properties and reduced acceleration values, probably due to partial degradation occurs. As a general trend, aging under natural outdoor complex conditions (i.e., oxygen, temperature, moisture, and UV light) would induce polymer chain fracture, partial degrading, and/or crosslinking.

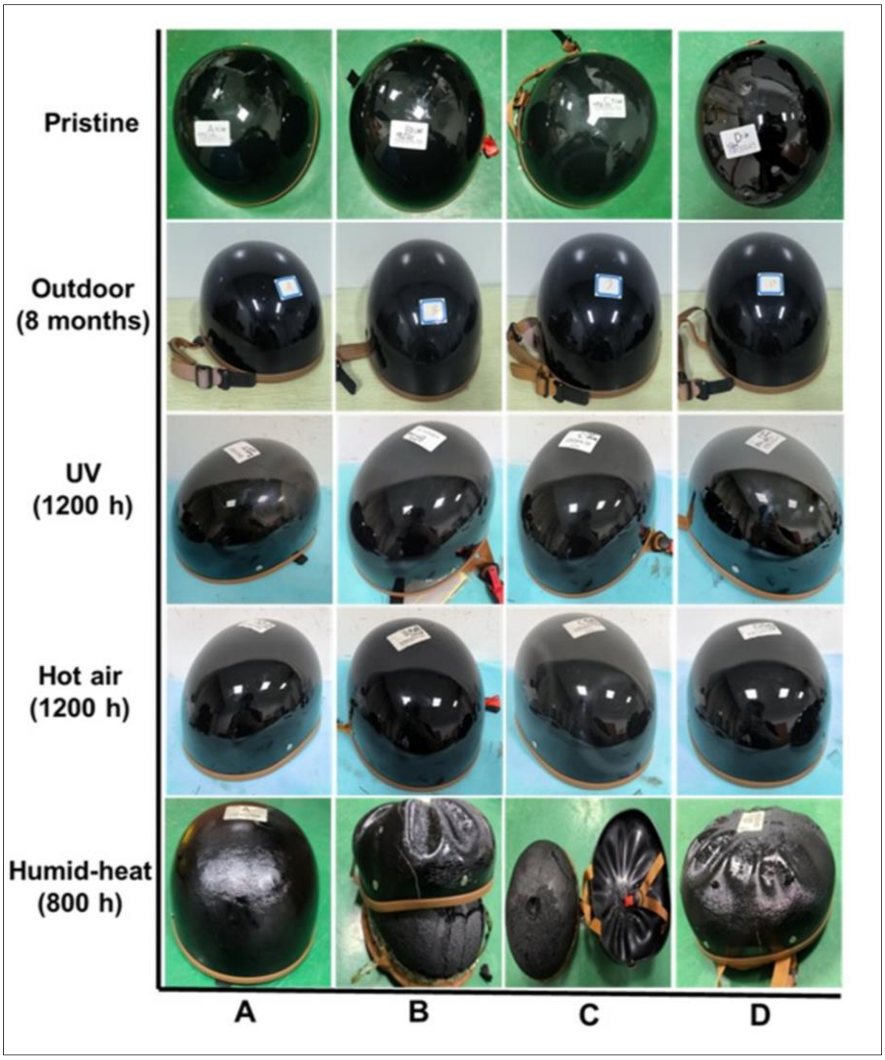

Figure 1. Photographs of the appearances of the helmets after different test conditions

As shown in Figure 2d and 2e, in occrdance with the previous results, four group helmet samples showed similar peak acclearation values as the pristine helmet, revealing the good impact resistance properties under the examined conditions. Moreover, the performance tested after long-term (1200 h) aging was similar to that tested after short-term (100 h) aging. Therefore, regardless of the helmet composition, the effect of UV-light and hot air flow on the aging of helmet shells were negligible. The promising results may be ascribed to the fact that the penetration of UV-light or the diffusion of oxygen during the aging process is limited due to the presence of coating and the condensed polymer morphology.

However, once the helmet samples were treated under humid-heat condition, the distinct different performances were found from the pristine for all four samples (Figure 2f). The acceleration values of the type-B and type-C helmets dropped significantly. In addition, the time factor of the helmet's exposure to humid-heat condition was also amplified. For an aging duration of up to 800 h, the acceleration values of the type-B and type-C helmet reduce nearly half of the pristine. Under humid-heat condition, outer shell materials suffered from thermo-oxidation degradation that was possibly induced by the hydroperoxides or radical scavengers [20].

The rigidity of the helmet is also investigated as an important factor for their practical appliaction. It is speculated that the aging process may change the stability of the helmets, in turn changing their protective performance. The outer shells may be considered to function independently of the stability because of a thick sponge buffer layer attached to the underside of the shell.

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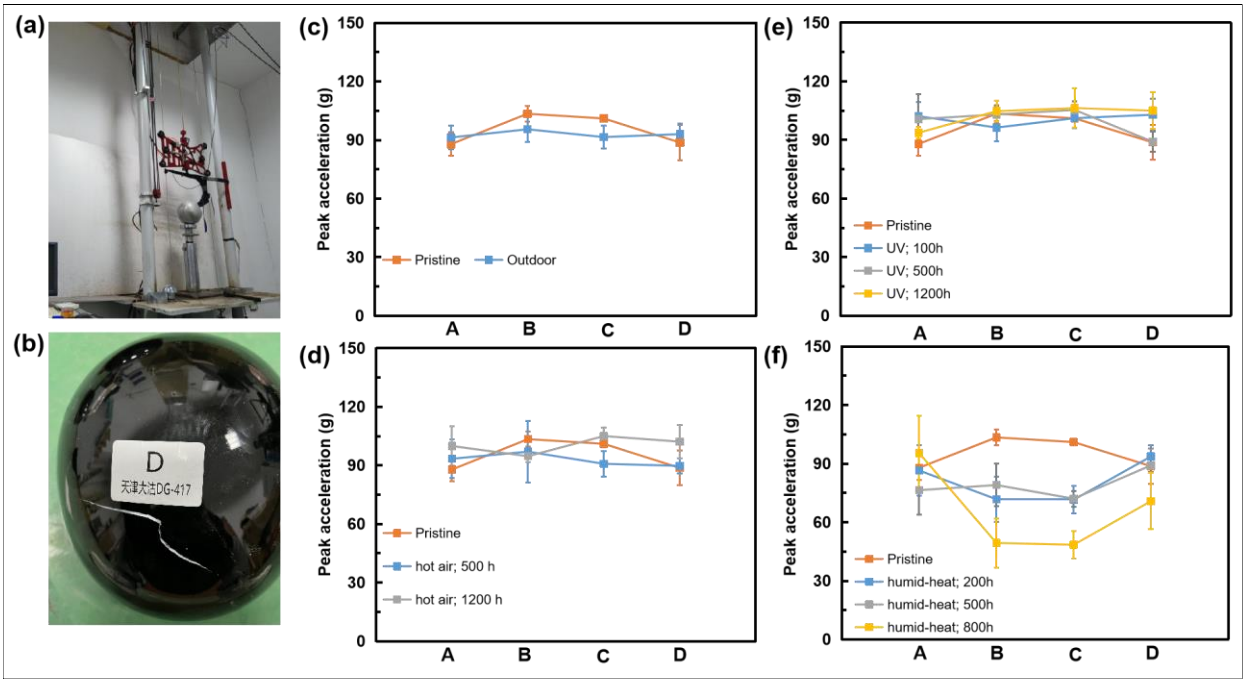

Figure 2. Peak acceleration (g ± SD) of impact tests at three points for helmets aged under (a) drop tower impact testing system, (b) lateral deformation testing machine, (c) outdoor, (d) UV, (e) hot air, and (f) humid-heat conditions. g= 9.80665 m s^{-2}

In Table 1, the pristine helmets exhibited similar lateral deformation (36.0-39.4 mm) and residual deformation (10.4-12.5 mm) values. The lateral deformation values were slightly enhanced after aging under UV-light or hot air flow conditions. These changes might be ascribed to weak phase separation and loss of rigidity induced by cross-linking and chain scission. On the other side, relatively smaller residual deformation values were recorded for aged helmets, indicating either significant residual stress existed or permanent distortion occurred. In particular, helmets aged under humid-heat condition exhibited significant differences: both lateral and residue deformation values were decreased. After humid-heat aging, the lateral deformation values decreased due to cross-linking and hardening of polymer phases. Differently, the decreased residual deformation values were consequently of the loss of its elastic behavior. The above result suggested all the helmets before and after aging nearly meet the practical critical, aside from the poor appearance acquired under humid-heat conditions.

Table 1. Stiffness test of helmets aged under different conditions at the selected duration[a]

Sample		Type-A	Type-B	Type-C	Type-D
Pristine	Lateral deformation[b]	38.8	36.0	39.2	39.4
	residual deformation[c]	12.5	10.4	12.5	11.7
UV; 1200 h	Lateral deformation	40.2	38.7	39.8	44.7
	residual deformation	11.4	10.4	12.1	11.7
Hot air; 1200 h	Lateral deformation	38.8	40.5	41.3	39.7
	residual deformation	8.3	10.2	10.2	8.3
Humid-heat; 800h	Lateral deformation	30.3	15.8	9.6	17.6
	residual deformation	3.20	1.46	0.62	2.52

[a] Numbers were averaged from 2-3 measurements. [b] Data was recorded by measuring the deformation at initial 30 N and 630 N.
[c] Data was recorded by measuring the deformation at 630 N and retract 30 N. Note: the lateral deformation and residual deformation should be less than 40 mm and 15 mm, respectively.

Subsequently, measurements of the deformation at elevated temperatures were also carried out to further assess the stiffness properties of the helmets under humid-heat condition. The recorded heat deflection temperature values were compared in Figure 3. Apparently, the pristine samples (black pillars) showed marginally enhanced values than the aged samples. This suggested that aged samples have gone through forms of morphological changes, which did not have much effect the overall thermal mechanical properties. The results agreed with the above-mentioned characterizations. Type-A helmet samples exhibited much higher thermal stiffness compared to the other three types because of the presence of high amounts of polycarbonate fractions.

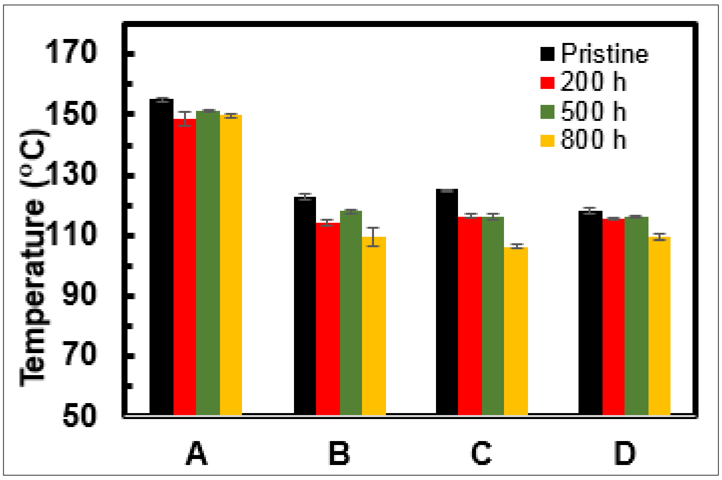

Figure 3. VICAT softening temperature for pristine samples and samples aged under humid-heat condition for different time duration

In order to further reveal the underlying deterioration mechanism under humid-heat conditation, SEM was applied to analyze the surface morphology of the helmets. Figure 4a and 4b compared the pristine and type-B helmet after humid-heat treatment. Clearly, the pristine helmet showed a dense layered structure, which endowed the helmet sharing great stress transfer effect when suffering impact. However, after 800 h humid-heat aging process, the fracture surface of type-A helmet were much looser than the pristine surface and an increase of the microporous structure was observed. This morphlolgic changes facilitated the penetration of the stimuli (UV, moisture, etc.) as well as the defact propagation during impact tests.

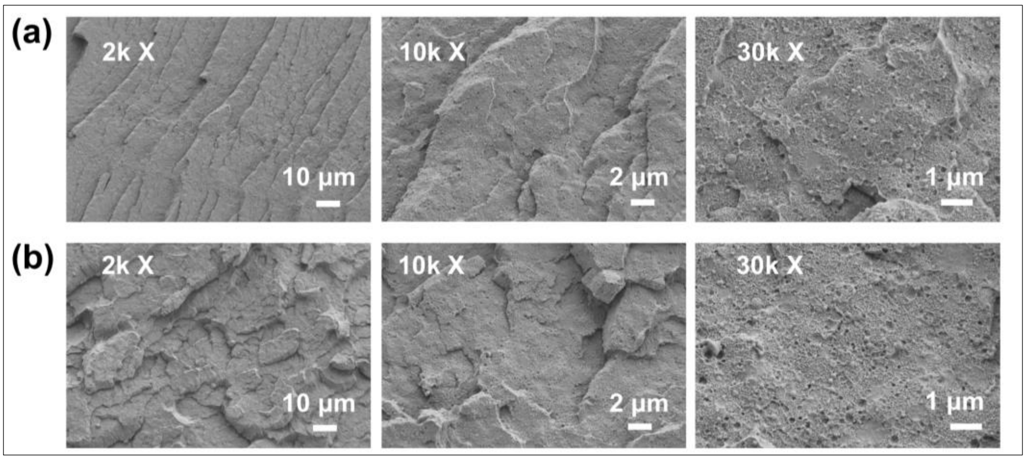

Figure 4. SEM micrograph of fracture surfaces of specimens (a) pristine type-B helmet and (b) aged type-A helmet under humid-heat for 800 h

The change of mechanical in ABS is often assigned to the chain degradation in the polybutadiene phase and a corresponding change in chemical structures would be expected. Therefore, the effect of humid-heat aging were analysed in Fourier transform infrared (FTIR) spectra in Figure 5. For type-A sample, the absorbance at ~2236 cm^{-1}, 1731 cm^{-1}, and 1636 cm^{-1} were assigned to cyano groups, carbonyl groups and butadiene units, respectively, confirming the co-exist of ABS and PC phases. After aging for 800 h under humid-heat condition, the spectra signals showed increases in carbonyl bands and decreases in butadiene bands after normalized, considering aging of polybutylene chains (Figure 5a). For the other samples, similar trend in the changes of the absorbance at 1731 cm^{-1}, and 1636 cm^{-1} was presented (Figure 5c-5d). The FTIR analysis provided information regarding the nature of surface chemicals of pristine samples and aged samples. According to the above analyses, humid-heat aging accelerates the breakage of polybutadiene chains: on the one hand, this reduces the mechanical properties and gloss of the helmet; on the other hand, the secondary cross-linking process increases the brittleness of the helmet.

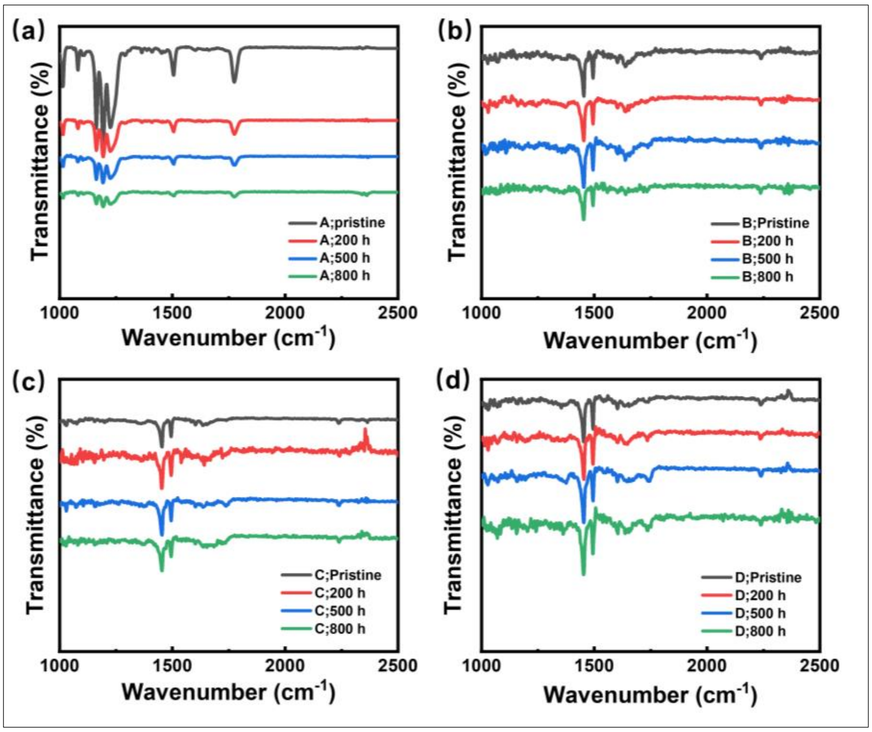

Figure 5. FTIR-ATR scanning of the four types of helmets aged under humid-heat condition. (a) Type-A samples; (b) Type-B samples; (c) Type-C samples; (d) Type-D samples

Furthermore, differential scanning calorimetry (DSC) was used to analyze the aging effect on intermolecular interaction. All helmets were treated under humid-heat condition, and endothermic curves after erasing thermal history were presented in Figure 6. In the first heat scan the non-reversible endothermic peaks might present due to the presence of residue stress and aged by-products. In the second heat scan, the glass transition temperature values (T_g) for type-A samples were all located at ~111°C and ~145°C (Midpoint) (Figure 6a), corresponding to amorphous styrene-acrylonitrile (SAN) phase and polycarbonate phase, respectively.The bimodal feature was caused by the partial immiscibility of polymer phases [21]. The polybutadiene phase was unable to detect in the selected temperature region, which should only available at around -85°C. It should also note that aging might induce chain scission and lead to reduced T_g and changes of surface functionalities. However, the aged samples showed similar thermal behavior compared with the pristine sample. The most noteworthy change was the minor shift of T_g of the polycarbonate phase from ~143.5°C to 142°C. The result indicated that aging induced small changes in short-range order, which affecting the impact resistance and rigidity performance but not the long-range interaction in polymer systems. The above results were also applicable for the other three types of samples, where each type of aged samples showed similar endothermic curves and spectra. Among these samples, the T_g of SAN phases showed negligible temperature shifts from 111°C to 109-110°C. Though, type-B and type-C samples showed strange exothermic peaks at around 143-144°C (Figure 6b and 6c), assigning to the decay of excess enthalpy due to the presence of cross-linked region or fillers in the polymer matrix [22, 23]. The thermal behavior of aged samples at different humid-heat durations was close to the thermal behavior recorded from the pristine samples.

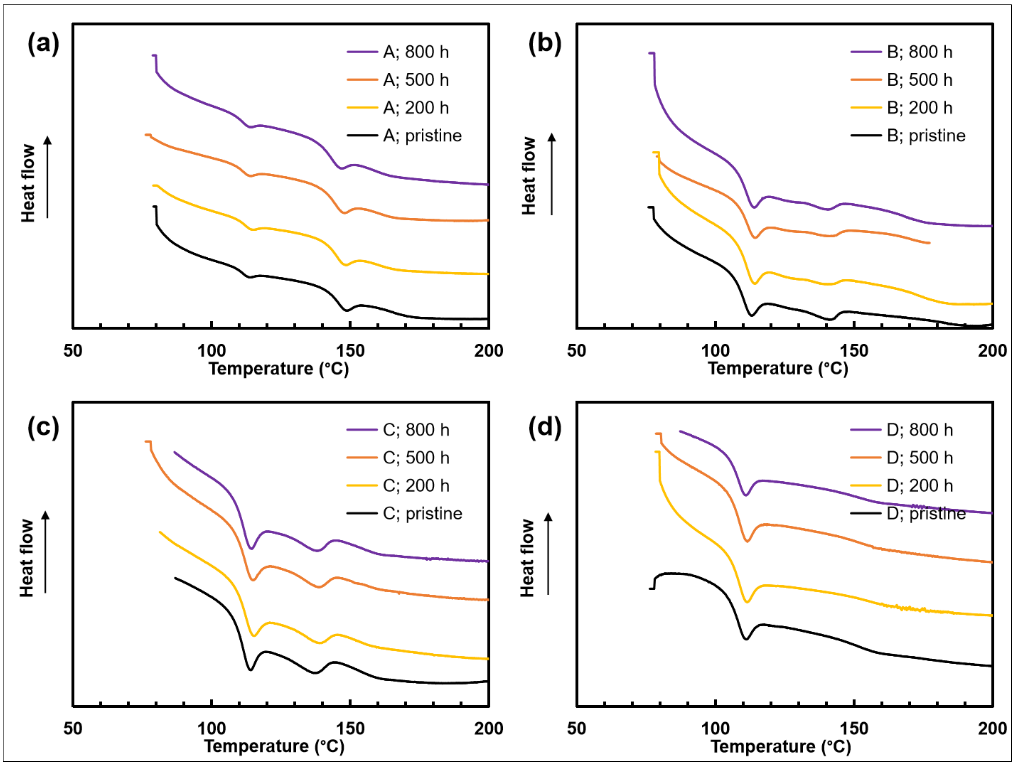

Figure 6. DSC curves of 2nd heating of specimens aged under humid-heat condition. (a) Type-A samples; (b) Type-B samples; (c) Type-C samples; (d) Type-D samples

The glass transitions of the polymers were comfirmed by dynamic mechanical analysis (DMA). The storage modulus (Figure 7a) and loss modulus (Figure 7b) obtained by DMA were presented for the representative samples aged under humid-heat condition. It showed a small peak shift from initial 112.5°C to 109.8°C (aged for 800 h), meanwhile the storage modulus decreased from 1825 MPa to about 1325 MPa (aged for 800 h). Changes of both parameters increased with aging time. The results confirmed that degradation and cross-linking after humid-heat aging led to stress hardening and general softening, resulting in the decreased stiffness, reduced modulus, enhanced peak acceleration, and slightly reduced glass transition, meaning the commercial helmets still afford good protective performance even after severe aging.

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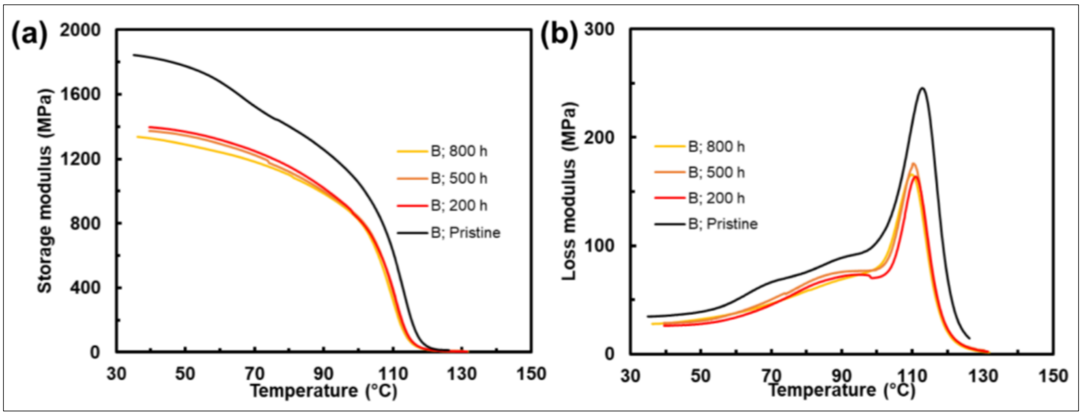

Figure 7. DMA curves of type-B specimens aged under humid-heat condition.
(a) Storage modulus; (b) Loss modulus

Additionally, complete thermal decomposition was presented in Figure 8. The onset temperature of pristine sample was about 5°C higher at the Tmax, compared with the aged samples. All aged curves showed nearly overlapped feature with some variations. This suggesting aged sample still showed high thermal stability as pristine.

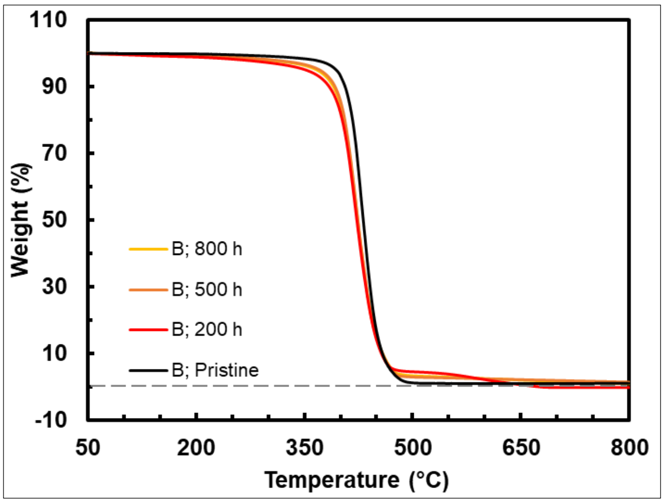

Figure 8. TGA curves of type-B samples after humid-heat aging for different time periords

4. Conclusions

In this work, the physical performance of aged commercial helmets was investigated. The results of impact test and stiffness measurements showed that helmets aged under outdoor, UV, and hot air flow conditions were able to deliver a competitive peak acceleration values, lateral and residue deformation values at practical conditions, compared to their pristine helmets. However, all helmets showed obviously decrease in impact strength, gloss, and stiffness under humid-heat conditions. From the obtained thermal analysis results, used to determine the changes of the polymer interactions and stability, it can also conclude that the single aging had minor influence on the changed of the performance except humid-heat aging. The details of the polymer chain aging requires further study since it might be of importance for the explanation of the obtained properties. Based on the carried out tests and results, the outer shell of the helmets can still play a role in practical application.

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