Experimental study on mechanical property and stone-chip resistance of automotive coatings

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Abstract

The damage of automotive coatings caused by stone impact is a problem that has attracted great attention from automotive companies and users. In this work, experiments were conducted to investigate the dynamic tensile properties and stone-chip resistance of automotive coatings. Four kinds of paint films and three typical coatings (single-layer electrocoat coating, single-layer primer coating, and multilayered coating) were used. Under dynamic tensile load using split Hopkinson tension bar (SHTB), the engineering stress-strain curves of the paint films at medium and high strain rates (from 50 to 600 s−1) were obtained. Results indicated that the mechanical properties of the paint films exhibited strong nonlinearity and strain-rate correlation. A modified anti-impact tester was used to complete repeatable single impact tests. The effects of some key parameters, i.e., impact velocity, impact angle, and paint film thickness, on the stone-chip resistance of coatings were systematically investigated. The influence of contact type under high-speed impact conditions was investigated as well. The surface morphologies of the coatings after impact were examined by scanning electron microscopy (SEM), and the failure mechanism of the coatings under normal/oblique impact was discussed. In all experiments, the paint films showed brittle fracture behavior.

1. Introduction

Automotive body coatings (multilayered coatings for short herein) are a typical multi-layer composite structure. Generally, a coating system is composed of a metal substrate, a pretreatment, an electrocoat (CED), a primer, a basecoat and a clearcoat [1]. Coatings play a significant role in automotive aesthetics and part protection. Particularly, parts underneath a vehicle that are vulnerable to stone impact are coated with CED with a thickness of hundreds of microns, which provides them with stone-chip and corrosion resistance [2, 3].

At present, automotive coating performance is mainly evaluated by using experiment and simulation [4, 5]. For experimental studies, two problems are mainly investigated, namely the scratch resistance [6, 7] and stone-chip resistance. Several theories about coating failure due to impact have been proposed [8–10].

Compared with multi-particle impact tests, single-particle impact tests are of good reproducibility, which therefore are more attractive. Impact-induced coating damage is typically characterized by two failure patterns, namely, in-ply fracture and delamination. This complex phenomenon shows dependence on many external factors, e.g., impact velocity, impact angle, paint film thickness, contact type, and temperature. Some researchers have studied the effects of external factors on the stone-chip resistance of automotive coatings. By using a controlled accelerated stone thrower (CAST), Buter [11] found that the coating failure mode is related to contact type under impact. Ramamurthy [12] found that a higher impact velocity will aggravate coating delamination, and wet coating is less damaged due to plasticizing effect of water. Zehnder et al [13] measured the temperature rise of the coating during impact, and found that the peak temperature is as high as 200 °C, which exceeds the glass transition temperature of the coating. The stone-chip resistance of coatings is related to their mechanical property and DOI.
properties. It is reported that weathering affects the performance of coatings, and long-term weathering results in poor stone-chip resistance of coatings [14]. Lonyuk et al [15, 16] developed a single-impact tester, which could change the projectile velocity, impact angle and test temperature in a wide range. They studied the effects of primer crosslinking agent content and glass transition temperature, and pointed out that the removal of the coating is affected by the combination of impact velocity and temperature. On the other hand, automotive coatings are polymer coatings. Some researchers have investigated the damage behavior of polymer coatings under impact loading [17, 18]. Although the single impact test has been proven to be a repeatable method for studying the stone-chip resistance of coatings [15], for unavailability of state information, investigation of the influence mechanism of these factors is limited, and the studies regarding impact failure mechanisms of coatings are still scarce.

Under different conditions, automotive coatings exhibit different impact failure behavior, which is closely related to the coating properties. However, in the literature, there were few experimental investigations involving the mechanical properties of a single film of automotive coatings. During impact, the strain rate of the materials can reach as high as $10^3 \text{ s}^{-1}$ [12]. Therefore, studying the mechanical properties of the coating films under impact condition is also an indispensable task.

Polymer has a nature of tension-compression asymmetry. For purpose of determining complete stress-strain characteristics of the material, uniaxial tests in both tension and compression are usually required. Unlike bulk polymers, automotive coatings are polymer films with micron thickness. In consideration of size effect [19, 20], general test methods, e.g., nanoindentation [21, 22] and split Hopkinson pressure bar (SHPB) [23–26], for bulk materials are not appliable to these films.

The split Hopkinson tension bar (SHTB) test is a well-known experimental method to characterize the mechanical properties of materials under high-speed deformation [27]. Some researchers have studied the dynamic tensile properties of various types of polymers via using SHTB method [28–31]. However, in the aforementioned studies on the mechanical properties of polymers, the specimens were in dimensions above millimeters, which does not match the micron thickness of coating films. The compression behavior of automotive paint films at high strain rates was studied in [32], but the specimens used were stamped from stacked paint films, therefore, the obtained mechanical properties are not accurate.

In light of the two issues mentioned above, in this study, dynamic tensile tests of paint films were performed, based on which, single impact tests were conducted to evaluate the stone-chip resistance of several typical automotive coatings. Dynamic tensile tests of the paint films are introduced in section 2. Single impact tests are presented in section 3. In section 4, experimental results are discussed, and failure mechanisms are analyzed. Finally, a conclusion is drawn in section 5.

### 2. Dynamic tensile test by SHTB

#### 2.1. Paint films of automotive coating

Four kinds of paint films (i.e., CED, primer, basecoat and clearcoat) are studied, and the parameters are listed in table 1, where the thickness of the films was measured by the DELTASCOPE gauge produced by FISCHER, Germany, and the density was measured by the Dahometer DH-300 electronic densitometer.

#### 2.2. SHTB

Medium and high strain-rate tensile tests at engineering strain rates from 50 to $600 \text{ s}^{-1}$ were carried out using the SHTB technique to obtain the engineering stress-strain relation of automotive paint films.

Figure 1 shows a schematic of the SHTB device. The airflow drives the bullet to hit the flange/steel bar at a certain velocity. The flange gains kinetic energy and then hits the discharge bar, after which, they move together. Finally, the kinetic energy of them is completely absorbed by the energy absorber. The function of the steel needle is to keep the two bars level. The impact velocity of the bullet is controlled by the air pressure, which further influences the incident stress pulses, that is, a higher the air pressure leads to a higher the strain rate in the film specimen.
In light of the problem of impedance matching, the incident and transmitted bars made from PMMA are used. A copper pulse shaper is placed on the end face of the flange to relieve the impact of the bullet, which increases the rise time of the incident pulse signals and delays the arrival of the peak stress. Simultaneously, instead of the traditional metal strain gages, high-sensitivity semiconductor strain gages are installed on the surface of the PMMA bars, for the sake of accurately capturing the strain signals in the transmitted bar. In addition, the Pattex PSK6C glue is used to connect the specimen with the incident and transmitted bars, respectively. The SDY2107A ultrahigh dynamic strainometer and a data collector are used to record the strain signals.

In this SHTB device, the PMMA incident and transmitted bars have the same size, with a length of 1200 mm and a diameter of 12 mm. The steel bar is 2760 mm in length, and its diameter is 19 mm. The thickness and diameter of the flange are 45 mm and 27 mm respectively.

2.3. Method
The incident strain $\varepsilon_i$, reflected strain $\varepsilon_r$, and transmitted strain $\varepsilon_t$ were recorded as a function of time $t$, which is achieved by using two semiconductor strain gages G1 and G2 attached to the surfaces of the PMMA incident and transmitted bars, respectively. The main component of automotive coatings are cross-linked resins (glassy amorphous polymer), which display obvious brittleness at ambient temperature [13]. According to the one-dimensional elastic stress wave theory [33], the engineering strain rate, strain and stress in the specimen can be calculated through:

$$
\dot{\varepsilon} = \frac{c_0}{L} (\varepsilon_i - \varepsilon_r - \varepsilon_t)
$$

$$
\varepsilon = \frac{c_0}{L} \int_0^t (\varepsilon_i - \varepsilon_r - \varepsilon_t) \, dt
$$

$$
\sigma = E \frac{A}{A_t} \varepsilon_t
$$

where $c_0$ is the longitudinal wave velocity in the tension bars; $L$ is the gage length of the specimen; $E$ is the Young’s modulus; $A$ and $A_t$ are the cross-sectional area of the incident/transmitted bar and of the specimen, respectively.

2.4. Specimens
The width of the specimens cannot exceed the diameter of the PMMA bars. In addition, there are limitations on the selection of specimen gage length [30]. Therefore, according to the waveform obtained in the pre-test, the
size of specimen needs to be determined as accurately as possible, so that the strain rate of the specimen can reach a stable state. The dumbbell-shaped specimens shown in figure 2 are used.

3. Single impact test

3.1. Impactors
From the perspective of repeatability in single impact tests, 2 mm-diameter spherical steel particles (0.033 g each) are used, with the tensile strength and yield strength of 520 MPa and 205 MPa, respectively. In order to control variables, a steel grit particle (0.228 g) with three different shapes from standard DIN 20567–1 is selected.

3.2. Coating samples
One coating sample represents a complete coating system. Three kinds of coating samples are studied (see figure 3): single-layer CED coating samples (150 mm × 70 mm), single-layer primer coating samples (150 mm × 70 mm) and multilayered coating samples (200 mm × 100 mm). The paint film thickness of the two single-layer coatings can be controlled during the robot spraying process.

The substrates of these samples are cold-rolled steel sheet with the same thickness of 0.85 mm, and its tensile strength and yield strength are 370 MPa and 235 MPa [34, 35], respectively.

It must be noted that all the paint films and samples were stored in a dry box, and all tests in this study were performed at ambient temperature.

3.3. Multifunctional anti-impact tester
The tester is shown in figure 4. The gas tank serves to stabilize the air pressure during impacting. The tester can work continuously under a given working pressure (0–0.5 MPa). A rotatable clamp is installed in the cavity, therefore, the impact angle (the angle between the impact direction and the sample plane) and the distance from the spray gun outlet to the coating sample are adjustable. The coating sample is clamped by two parallel steel bars.
and a steel disk. The vibrating machine and the feeding tray can feed impactors automatically into the spray gun within a given time.

Under each condition, a test is repeated five times to eliminate randomness. The typical phenomenon with the highest repeatability is regarded as the final result.

3.4. High-speed camera
In the impact tests, the impact velocity of particles is determined by a working pressure. The frame rate of the high-speed camera and the displacement of the tracked particle are used to calculate the velocity at which the particle impacts the coating sample. Moreover, the high-speed camera captures the contact state of the impactor when it hits the coating sample, thus the contact type is determined. In this study, the Phantom VEO 410L high-speed camera with an AT-X M100 PRO D lens was used to track and record the movement of particles. The impact velocity of the 2 mm-diameter spherical steel particle under various working pressures is shown in figure 5.

4. Results and discussions

4.1. Dynamic tensile properties of paint films
Four kinds of paint films were tested at different strain rates (50, 150, 300 and 600 s⁻¹), but for the convenience of explanation, only the strain gage signals and strain rate history of the clearcoat film at the highest strain rate (600 s⁻¹) are discussed here. The strain gage signals recorded on the incident/transmitted bar are plotted in figure 6. Smooth transmitted pulses with high signal-to-noise ratio ensure the accuracy of the results. The transmitted signals indicate that the specimen fails within 2 × 10⁻⁴ s. The local waveforms of the incident/ reflected signals and the engineering strain rate history of the specimen are depicted in figure 7 and figure 8, respectively. Although the curves of the incident/reflected pulses do not have a horizontal stage, they reach a stable state [28] within a few hundred microseconds. It is observed that the strain rate of the material increases rapidly from 0 to 500 s⁻¹ during the deformation process, and then levels off to about 600 s⁻¹. As a consequence, the specimen is viewed to deform at a constant strain rate.

The dynamic tensile results of the paint films at strain rates of 50 s⁻¹ and 600 s⁻¹ are shown in figure 9. The fracture of materials occurs in the uniform part of the specimens, and the ridge-like cracks are generated. In fact, during the tests, many fragments were scattered on the SHTB device when a specimen was broken. The number of the fragments reaches the maximum at the highest strain rate of 600 s⁻¹. The results prove the brittle fracture behavior of the paint films under dynamic tension.
Figure 10 presents the tensile engineering stress-strain response of the paint films from medium to high strain rates. The response of each kind of paint films shows strong dependence on strain rate. Under most conditions, all the paint films show pre-peek nonlinear behavior before peak stress \[36\]. And the nonlinearity increases with the increase of strain rate. Fiedler et al and Morelle et al \[37, 38\] pointed out that under tensile load, these kinds of glassy polymers will fracture before peak stress, and there are no softening and rehardening behaviors like that shown under compression, which is consistent with the results in this study. At all strain rates, the paint films fail rapidly after reaching the peak stress, and exhibit little plastic behavior. Since the paint films fail at small strain, the true stress is close to the engineering stress. According to the results exhibited in figure 10, an increasing strain rate results in the decrease of failure strain (defined as the strain corresponding to the peak stress), but the increase of tensile strength (namely peak stress) and the overall stiffness of the paint films.

4.2. Influencing factors on the stone-chip resistance of coatings

For convenience, the single-layer CED coating with a thickness of 19.9 μm is named CED-19.9. This designation for specimens is applied to the single-layer primer coatings and multilayered coatings, e.g., Primer-33 and Multilayer-114.5.
4.2.1. Impact velocity

In this study, the critical velocity is defined as the velocity above which the paint films can be torn off by the 3M adhesive tape after impact. The failure patterns of the coatings after normal impact by the spherical particle are compared in figure 11 (an optical microscope was used). The indentation of a high-speed particle does not delaminate the coatings at the center of the impact zone, but presses the coatings herein on the substrate tightly, forming a disk shape delamination-free region. The formation of the disk shape is similar to the failure mechanism of the punching process [39, 40]. Spherical steel particle is equivalent to a punch, and the outside area of the disk shape in the substrate is equivalent to a mould. In this way, the disk shape is formed. Although the paint films, CED-19.9 and Primer-33, vary in category and thickness, they exhibit similar failure patterns, that is, the paint films delaminate in a ring shape. The Multilayer-114.5 is slightly different from the above two coatings. In addition to the ring-shaped buckling area, the center of impact zone collapses inward, which may be related to the difference of thickness and structure between different coatings. In fact, when the velocity increases to a certain value, the damaged coating of each system will automatically peel off after impact. But the common regularity of all coating systems is that the failure patterns do not change with impact velocity. Figure 12 shows the dependence of damage area diameter of the coatings on normal impact velocity. For these three different coating systems, below the critical velocity, the increase of velocity results in the increase of the diameter of the damage area, which remains valid even if the velocity exceeds the critical one. However, the increase is quite
Figure 9. Dynamic tensile results of (a) clearcoat, (b) basecoat, (c) primer and (d) CED at the strain rate of 50 s$^{-1}$ and 600 s$^{-1}$, respectively.

Figure 10. Tensile engineering stress-strain curves of (a) clearcoat, (b) basecoat, (c) primer and (d) CED paint film at different strain rates (50–600 s$^{-1}$).
Figure 11. Typical damage area of (a) CED-19.9, (b) Primer-33 and (c) Multilayer-114.5 after impacted normally by a 2 mm-diameter spherical steel particle at different velocities.

Figure 12. Damage area diameters of the coatings at different velocities under 90° impact.
weak. In other words, impact velocity of the spherical steel particle significantly affects the damage degree of the coatings, rather than the size of the damage area.

4.2.2. Impact angle
We study the effect of impact angle by redoing the impact tests on different coatings with a spherical particle at the corresponding critical velocities, with the results shown in figure 13.

At the impact angle of 60°, the lip areas of CED-19.9 and Primer-33 show obvious material piling up, and the coatings on the outer side of the lip buckle (according to shadow) and fracture severely. When the impact angle decreases, the shape of central area changes from a disk to an arc. The lip is more severely damaged, and even large area delamination occurs. It is worth noting that at the impact angle of 30°, a large number of radial cracks are generated at the center of the impact zone of Primer-33, while the CED-19.9 seems to fail in a ductile way. According to the SHTB tests, the overall stiffness of the CED paint film is larger than that of the primer, so the CED-19.9 has better performance in resisting fracture. For Multilayer-114.5, as the impact angle decreases, the overall damage area is significantly reduced. It is found that the paint films of the multilayered coating could not be torn off using 3M adhesive tape. It means that when the coating is subjected to an oblique impact, the damage of coating-substrate interface decreases. Therefore, for all the coating systems, the overall damage degree will be reduced when subjected to oblique impact.

4.2.3. Paint film thickness
At the critical velocity, a 2 mm-diameter spherical steel particle was used for normal impact test on the CED-14 and CED-25, and the results are presented in figure 14. The results show that, within the studied paint film thickness, a thicker CED leads to an increased size of the overall damage area, that is, the stone-chip resistance of the coating decreases, which is contrary to intuition. In addition, the diameters of the disk-shaped area of the CED-14 and CED-25 decrease with the increase of the thickness of CED, and seem to have a tendency to drop to zero. That is to say, the disk may disappear with the increase of paint film thickness. Therefore, it is speculated that the change of thickness will influence the failure pattern of the polymer coatings under the impact of a spherical steel particle. In order to further verify the above inference, a normal impact test was carried out on the Primer-55 at the critical velocity, and the result is shown in figure 15. Compared with Primer-33, size of the overall damage area increases, and the coating at impact center no longer adheres to the substrate, but exhibits crater-shaped phenomenon similar to that in figure 11(c). This result simultaneously verifies the guess in section 4.2.1.
Although the impact of the coatings is a transient process, the failure mechanism can be explained by quasi-static indentation \([8, 10]\). If the coating is thin enough, the interface shear stress has a small value, as a result, the coating-substrate interface is less likely to fail, which brings about a small damage area of the coating. As the thickness of the film increases, the strain energy in the film that serves as the driving force for crack growth will increase, leading to an increased damage degree of the coating \([41, 42]\). However, the critical thickness restricts the infinity of the positive correlation \([43]\). When the paint film thickness is thick enough, the kinetic energy of the impactor is almost completely absorbed by the film, at this time the degree of coating failure decreases with a larger thickness.

4.2.4. Contact type
An irregular steel grit from DIN 20567–1 is selected, which is characterized with a sharp, linear and ellipsoidal shape. The Multilayer-114.5 is repeatedly impacted at a relative high velocity \((50 \text{ m s}^{-1})\), and the contact type is determined by the high-speed camera. Figure 16 depicts the failure patterns of the Multilayer-114.5 under three different contact types. For point impact, a large number of radial cracks are generated in the impact zone, and irregular cohesive failure zones are formed after the cracks propagated. When edge impact occurs, along the edge of the steel grit, an obvious linear crack is generated in the coating. And there exists another linear crack perpendicular to the former and run through it, which forms a butterfly-shaped broken zone. As for ellipsoid impact, the failure pattern is similar to that caused by a spherical particle. However, due to an uneven stress distribution, a large number of radial cracks are generated in the buckling area, and the coating near the lip delaminates severely. Under different contact types, the maximum sizes of the irregular damage areas are measured (see figure 17). Obviously, the ellipsoid impact at a high velocity will induced a large degree of damage because of uneven stress, which is contrary to what can be observed under low-speed impact \([11]\).

Figure 14. Typical damage area of (a) CED-14 and (b) CED-25 when subjected to the normal impact of a 2 mm-diameter spherical steel particle at the critical velocity.

Figure 15. Typical damage area of Primer-55 when subjected to the normal impact of a 2 mm-diameter spherical steel particle at the critical velocity.
4.3. Failure mechanism

4.3.1. Normal impact

Figure 18 shows the SEM photographs (including backscattered electron images) of the Multilayer-114.5 after normal impact at the critical velocity. A circumferential crack is observed on the crater contour (the top of the arched part), and several radial cracks appear outside, as shown in figure 18(a). At the center of impact zone, the coating fractures and a hole is formed (marked with yellow dotted circle); in the vicinity of the impact center, several radial large cracks are evenly distributed, and some chips are scattered on the coating surface, as shown in figure 18(b). Observing the hole with a higher magnification, the coating has fractured into a large number of irregular blocks without significant plastic deformation, as shown in figure 18(c). The coating exhibits different fracture morphologies, and the following conclusions can be drawn: (i) the coating fails in a brittle manner under impact; (ii) at the position of the crater contour, the coating is subjected to radial tensile stress, resulting in a circumferential crack; on the inside and outside of the contour, the coating is subjected to circumferential tensile stress, resulting in radial cracks. In particular, the center of impact zone is directly impacted by the spherical steel particle resulting in severely squeeze, thus more obvious radial large cracks are formed due to crack propagation.

Figure 16. Failure patterns of Multilayer-114.5 under (a) point impact, (b) edge impact and (c) ellipsoid impact at the high velocity.

Figure 17. Maximum size of damage area of the coatings under different contact types.
4.3.2. Oblique impact

Figure 19 shows the SEM photographs of the Multilayer-114.5 after oblique impact at the critical velocity. At 60°, significant material piling up along the impact direction and large cracks form in the impact zone, which is the result of both friction and extrusion. At 30°, large crescent-shaped cracks appear, the corresponding failure mechanism of which is similar to that under scratch, that is, bending-caused conformal cracks [44]. Note that in figure 19(a), a U-shaped crack is generated behind the particle, which is also the result of coating bending under oblique impact.

Figure 18. SEM photographs of Multilayer-114.5 at the critical velocity under normal impact.
5. Conclusion

In this study, a series of experiments were conducted to systematically investigate the dynamic tensile properties and stone-chip resistance of automotive coatings. The following conclusions are drawn:

(1) Under dynamic tension, the paint films are fractured in a brittle manner and exhibit strong nonlinear behaviors. The increase of strain rate leads to the decrease of failure strain of the paint films as well as the increase of tensile strength and overall stiffness.

(2) In the single impact test, when the coatings are subjected to the normal impact of a spherical steel particle, the variation of impact velocity does not change the failure patterns and the size of the damage area of coatings, but it significantly affects the damage degree. As the impact angle decreases, the overall damage degree of the coatings gradually decreases. The thicker the paint films, the worse the stone-chip resistance of the coatings; and the thickness of the paint films will change the influence of the metal substrate on the polymer films. Under high-speed impact, due to the uneven stress distribution in the coatings, the ellipsoid impact causes more severe damage than the point type.

(3) When the coatings are subjected to normal impact, cohesive failure takes place. Circumferential cracks and radial cracks are caused by radial stress and circumferential stress, respectively. Under oblique impact, the failure mechanism is similar to that under scratch.

Our future study will focus on the effects of strength of coating-substrate interface and coating structure. In addition, industrial CT scanners may be able to help detect the state of coating-substrate interface after being impacted.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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