Quality control of protective polymer coatings on metal by acoustic method

A I Krasheninnikov, A P Luchnikov, A A Nazarenko, G Yu Dalskaya and N I Chernova
Physical and Technological Institute, MIREA – Russian Technological University, Moscow, Russia

fisika@mail.ru

Abstract. An acoustic method for quality control of adhesive compounds of polymer coating on metal in the coating–positive system qualitatively characterizing the value of the adhesive bond is proposed. Ultrasonic measuring cell is considered as a resonant system, the parameters of which are determined by the properties of all the parameters of the layered structure at the same properties of the piezoelectric sensor and acoustic contact. The coating adhesion is evaluated on the basis of the parameters of the amplitude-frequency characteristics of the studied layered structure of the composite coating according to the humming dependences of the adhesion – reflection coefficient the wave. The technique allows to control the processes of polymerization of organic coatings in the process of their formation.

1. Introduction
In technological processes of formation and operation of polymer protective coatings it is necessary to assess the quality of adhesive strength and integrity of the layer on both metal and non-metallic properties [1–2]. There are methods of non-destructive testing of defects in composite materials where ultrasonic waves are used [3] also registration of electromagnetic radiation waves by material defects under pulsed mechanical action on the material [3-6]. It is also important to have a reliable method of rapid analysis of adhesion compounds of coatings on a hard surface for extreme operating conditions, especially when exposed to chemically aggressive media and high humidity.

Considered acoustic method of nondestructive testing of adhesive joints of polymer coating on the metal when it is swelling in a hostile environment and exfoliation of the magnitude of the reflection coefficient for the acoustic wave and its frequency spectrum in the coating–positive system qualitatively describing the magnitude of the adhesive bond system. To assess the adhesion of the metal-coating system used the method of ultrasonic spectroscopy: the study of amplitude-frequency characteristics (AFC) of layered composite materials.

2. Measuring cell diagram
As represented in the Figure 1 a measuring cell consisting of a substrate 1 on which a layer of protective coating 3 is applied is presented. Between them during operation or testing it is possible to form a thin transition layer 2, which affects the quality of adhesion of the coating to the substrate 1. On the outer surface of the metal substrate 1 there are separately combined ultrasonic piezo-sensors: 4
– emitter and 5 – receiver of the ultrasonic range. To create an acoustic contact, the sensors are fixed with epoxy resin. The cell can be considered as a resonance system, the parameters of which are determined by the properties of all these elements, including layer 2. Since the properties of the piezoelectric sensor and acoustic contact are unchanged (experimental condition) the value of the acoustic parameters of the system (wave resistance, absorption) will be determined by the physical and chemical properties of the coating 3 and layer 2.

![Figure 1. Block diagram of acoustic control of adhesive strength metal–polymer compounds.](image)

In the above cell piezoelectric transducers with the main resonance frequency of 1.5 MHz were used for longitudinal waves and 7 MHz for shear waves. From the electrical point of view, the system can be represented as a quadripole, the properties of which are determined by the parameters of layer 2 and the properties of the coating. This makes it possible to investigate the frequency response of the cell using standard devices.

Like the base of the setting device taken AFC the type XI-47 (7 and 8 in Figure 1). It allows you to measure AFC in the range 1...250 MHz. Other components of the installation are two broadband amplifiers 6 and 8 as well as recording device 10.

The signal from the generator 7 is fed to the amplifier 8 and then to the emitting piezoelectric element 4. From the receiving piezoelectric element 5, the signal goes to the amplifier 6 and the indicator 9 with further recording on the recorder 10. The speed of the recorder tape is synchronized with the scan of the indicator 9. This makes it possible not only to observe the AFC, but also to record them at the same time. With a small attenuation of the signal, the use of the amplifier 8 is not necessary, i.e. the signal from the generator 7 can be fed directly to the piezoelectric element 4. Generator 7 and the indicated 9 are an integral part of the device XI-47.

3. Quality assessment of adhesive strength

The quality of the adhesive strength of the coating is evaluated by the maximum values (the value of the amplitude $h_0$) of the observed spectrum AFC of the pure metal substrate at the eigenfrequency $f_0$ of the emitter (or multiple frequencies), as well as by the value of the same maximum in the presence of a polymer coating on the metal. When measuring the frequency response of the layered structure, the coating quality is carried out by changing the relative reflection coefficient $K$, which is the ratio of the maximum amplitude $h_0$ of the acoustic signal at the resonance frequency $f_0$ without coating to the value of the signal $h$ of the coating-metal system. Typical AFC curves are shown in Figure 2 (shear waves, $f_0 = 6.96$ MHz).

Figure 2 shows the frequency response of the layered structure of the metal–composite coating of the type VL-02, based on the polymer. Experimentally observed AFC at the time: 1 – immediately after coating; 2–2.5 [ks]; 3–7.2 [ks].

The reflection coefficient $K$ qualitatively characterizes the adhesive strength of the polymer–metal system and its value is lower then higher the adhesive strength. When applying the coating material on
a metal surface, the maximum value of the frequency response (Figure 2) varies depending on the coating parameters (layer thickness, physical and mechanical characteristics of the coating, etc.).

**Figure 2.** Typical amplitude-frequency characteristic of layered structure metal – composite coating.

The change in $K$ from the coating thickness $d$ occurs according to the harmonic law with the damping of the oscillation amplitude (Figure 3) which leads to ambiguity in the measurement evaluation. The uniqueness of the process of measuring the adhesive properties of the system for frequencies in the ultrasonic range of 1.6 MHz is achieved when the thickness of the coating is not lower than 2 mm at longitudinal waves sound waves and for shear waves at frequencies close to 7.0 [MHz] yields a value of about 100 [$\mu$m].

**Figure 3.** Graph of the reflection coefficient $K$ which characterize the adhesive strength of the polymer–metal system from thickness $d$ of the polymer coating.

Experimental studies were carried out on polymer films with a one-sided sticky layer whose adhesive strength with a steel plate was 1.5 [N/m]. Acoustic sounding was carried out on longitudinal ultrasonic waves with a frequency of 1.6 [MHz].

For these conditions a qualitative change (decrease) in the adhesive strength of the layered structure 1-2-3 was observed (Figure 1), which was characterized by an increase in the value of $K$: 0.64; 0.86; 1, which corresponds to the coating: – on the acetone-free metal surface; – on the oil surface, wiped with a cotton swab; – on a metal surface without coating.

The possibilities of the acoustic method for changing the working area of the $SP$ coating contact with the substrate, which is possible with partial peeling of the coating as in the curing process (gas and other inclusions) and in the process of operation, i.e. aging (discontinuity, destruction, etc.). Modeling of these processes was carried out by introducing various defects under the coating layer in the form of cylinders with a diameter of 100 [$\mu$m] and a length of 3 mm, or by mechanical detachment of the coating part (up to 10 [%] of $SP$). In the first case, when the number of layer-by-layer defects changes from 0 to 40, The $K$ value increases almost linearly from 0.65 to 0.82. With a discrete decrease in the contact area (by 10 [%] of $SP$) the $K$ value monotonically increases from 0.65 to 1 at $SP = 0$.

When curing the coating (polymerization when applied from a solvent) it is possible to control the maximum value of h frequency response (Figure 2), changing over time polymerization (Figure 4, curve 1).
The relative reflectance is assumed to be \( K = \frac{h}{h_o} \) and its value decreases during curing (Figure 4, curves 1 and 3) of the coating either increases with destruction (occurrence of pores, delamination, corrosion sublayer, etc.) of the coating (curve 4, Figure 4).

When exposed to the polymer coating solvent (curve 2, Figure 4) there is an increase in the value of \( K \). So when applying acetone to the surface of the coating and its removal by drying from the polymer, you can see the restoration of the available protective properties. In this case, the adhesive strength to the metal acquires the initial value. Training of the layered structure at increased humidity of 98 [%] and temperature leads to a violation of the adhesion of the coating to the substrate (curve 4, Figure 4).

![Figure 4](image)

**Figure 4.** The graph of the kinetics changes reflectance coefficient \( K \) the structure of the polymer substrate on the stage; 1 – curing polymer; 2 - impact on coating solvent (acetone); 3 – drying of the solvent in the coating; 4 – the destruction of the adhesive contact of the polymer substrate.

The considered method of diagnostics of adhesive strength allows to determine the adhesion – reflection coefficient \( K \) for the polymer – substrate system by the calibration dependences to fix the violation of the adhesion parameter of the coating layer. The proposed technique also allows to control the polymerization processes of polymer coatings during their formation with the maturation of the characteristic curing time of the polymer in the polymer–substrate system.

In Figure 5 there is a chart of the kinetic dependence of the reflection coefficient of the ultrasonic wave to characterize the degree of polymerization of the composition XC-413 on a steel substrate is presented.

![Figure 5](image)

**Figure 5.** The graph of the kinetics reflection coefficient \( K \) in the polymerization layer composition XC-413 on the surface of the substrate of steel.

By differentiating the function \( K \) in time an extreme value is found at which the characteristic value of the polymerization time \( t_0 \) of the composition is manifested.

4. **Piezoelectric sensor**

As the primary transducers of the ultrasound transducer was used with typical parameters is given in Table 1.
Table 1. The parameter of the piezoelectric transducer.

| Parameter                                      | Quartz   | PZT-19   |
|------------------------------------------------|----------|----------|
| The speed of sound, $10^{-3}$ (m·s$^{-1}$)     | 5.7      | 3.3...4.2 |
| Density, $\rho 10^{-3}$ (kg·m$^{-3}$)         | 2.65     | 7...7.3  |
| Impedance, $z = \rho c 10^{6}$ (kg·m$^{-2}$·s$^{-1}$) | 14...17  | 23...31  |
| Dielectric constant, $\varepsilon$            | 4...5    | 1100...1800 |
| Piezomodule, $d_{33} 10^{-12}$, Cl/N          | 2.31     | 75       |
| Piezomodule, $d_{33} 10^{-12}$, Cl/N          | ---      | 150      |
| The coefficient of Electromechanical communication, $k$ | 0.095    | 0.2...0.4 |
| Quality mechanical factor, $Q$                | $10^4$   | 300      |
| Curie point (°C)                              | 469      | 290...305 |

The sensor used the halves of the disk piezoelectric emitter as two surface-excited sensors: one as an ultrasound emitter 4 (Figure 1) and the other 5 as the wave receiver. Both halves are attached to the metal with epoxy resin with an interval of 0.5...2 mm between half-discs 4 and 5. The portable version of the sensor for rapid analysis of coatings is two halves of the half-discs 5 and 6 (Figure 1) converter which are placed in the housing of the dielectric. The acoustic contact of the sensors to the metal is carried out through an auxiliary oil layer (transformer or castor).

The proposed system for monitoring the adhesion state of coatings is characterized by a measurement error, which is determined by the amplitude measurement error of the device XI-47 and does not exceed 10 %.

5. Conclusion

Introduced acoustic method for quality control of adhesive compounds of polymer coating on metal in the coating–positive system qualitatively characterizing the value of the adhesive bond is proposed. Ultrasonic measuring cell is considered as a resonant system, the parameters of which are determined by the properties of all the parameters of the layered structure at the same properties of the piezoelectric sensor and acoustic contact. The coating adhesion is evaluated on the basis of the parameters of the amplitude-frequency characteristics of the studied layered structure of the composite coating according to the humming dependences of the adhesion – reflection coefficient $K$ the wave. The technique allows to control the speed of the polymerization process applied to the metal anticorrosion coating, qualitative change of adhesion (adhesion) of the coating-substrate system both in the process of curing and in the process of its operation (destruction).

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