Effect of nanosized oxide fillers on the adhesive strength of epoxy lacquer under scratching

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Abstract. The paper reports on the results of a comparative study of the adhesive strength of coatings made of unfilled epoxy lacquer and lacquers filled with nanosized TiO₂, SiO₂, and ZnO oxides, which have been obtained in scratch testing experiments. The coatings are applied onto an aluminum-magnesium alloy base. The value of specific elastic energy per unit area of the cohesion boundary is used as the measure of adhesion. Scratch testing is performed with conical Rockwell indenters on an attachment to a Zwick 2.5 testing machine. The coating modified with silicon dioxide proves to have the highest resistance to adhesive failure under local action among all the studied coatings based on epoxy lacquer.

1.  Introduction
Epoxy lacquers are fairly often used as protective materials in the construction industry [1]. Epoxy lacquer is a solution of epoxy, most often diane, resins based on organic solvents. Being affordable, this finishing material has high technical parameters, namely high moisture and alkali resistance, mechanical strength, and safety. Besides, these materials can be used for making putties and for finishing metallic and polymeric bases. Among the shortcomings of the lacquer is insufficient plasticity stemming from its structure and its constituents.

One of the methods for improving the properties (thermal, mechanical, theological, electrical, optical, etc.) of epoxy lacquers is introduction of various additives [2, 3]. Inorganic particles, e.g. titanium dioxide (TiO₂), aluminum dioxide (Al₂O₃), quartz (SiO₂), carbon nanotubes (CNTs), etc., can serve as fillers. Herewith, the final properties of an epoxy coating depend on a number of factors, such as the type and mass concentration of the additive, the size and distribution of the filler particles in the polymeric matrix, the nature of the interaction between the matrix material and the filler. Another important factor to determine the efficiency of using polymeric lacquers as coatings is evaluation of adhesive strength and the mode of failure in the coating–base system. Cracking in coatings decreases considerably their reliability and durability since it allows oxygen to penetrate easily to the metal base surface thus causing its severe oxidation. There are many different methods for determining adhesive strength. However, only a few of them have gained wide acceptance in practice. The simultaneous separation method implies normal separation under tension or shear (the mushroom method, the stud method, disk separation), separation by centrifugal force (the ultracentrifuge method), by vibration (the ultrasonic method), through inertia of a moving sample (the pneumatic gun method). What these methods have in common is that the breakaway force acts with concentration, and it is distributed uniformly over the adhesion contact area. The results are
represented by the ratio of the breakaway force to the area of the adhesivized film. The method of gradual exfoliation is based on the evaluation of the force of exfoliation (delamination) of adhesively bonded surfaces. Besides, the scratch testing technique is currently widely used. It implies that a coated sample is scratched with a hard indenter with the application of a constant or progressing load [4, 5]. Scratch test experiments are especially efficient in the case of studying adhesion in hard and brittle coatings, like epoxy lacquers. The effect of nanosized TiO₂, SiO₂, and ZnO oxides modifying ED-20-resin-based epoxy lacquer on the microhardness, creep, and elastic modulus of the resulting coating was studied in [6]. The aim of this paper is to investigate, in scratch testing, the effect of nanosized TiO₂, SiO₂, and ZnO fillers on the adhesive strength of coatings produced from epoxy lacquer based on ED-20 epoxy-diane resin, applied onto an aluminum-magnesium alloy substrate.

2. Materials and methods

The paper studies epoxy lacquer based on epoxy-diane resin of grade ED-20, with an epoxy number of 21.1%, produced by Ya. M. Sverdlov Plant, Dzerzhinsk. Commercial titanium dioxide (IV) (purity 99.5%, particle size 21 nm), silicon oxide (IV) (purity 99.5%, particle size 10–20 nm), zinc oxide (II) (purity 99.5%, particle size <100 nm), produced by Sigma-Aldrich, are used as the fillers.

To produce the compositions, we made a solution of the ED-20 epoxy resin in tetrahydrofuran (THF) and dispersed the oxides in it (10 wt%) with the use of a ball mill. The thus-produced lacquers were solidified by polyethylenepolyamine (PEPA) at 25 °C for 24 h. Plates of the AMg6 aluminum-magnesium alloy with the roughness Ra 710 nm determined with a WykoNT 1100 optical profilometer were used as a base for applying the coatings. The coating thicknesses h are found in Table 1.

The features of the adhesive and cohesive failure of the epoxy lacquer were studied in scratch testing with conical Rockwell indenters on an attachment to a Zwick 2.5 testing machine. A special table was placed into the workspace of the machine, on which an automated device for horizontal sample transfer was installed, with a sensor recording the horizontal displacement force. During the testing, the indenter moved vertically at a constant speed. The scratch test was performed until exfoliation appeared in front of the indenter. This technique enables one to study coatings under different contact conditions and thus to model operation conditions [7]. The indenter displacement and the normal force were recorded during the tests with the use of the regular capabilities of the device. The vertical force was fixed by a precise force sensor of the testing machine. The lateral force was read from the sensor installed on the moving table. All the data were synchronized.

| Coating                | h, mm | HM, N/mm² | \(E_{17}/(1-v_{s}^{2})\), GPa | \(F_{r}, N\) | \(F_{p}, N\) | S, mm² | \(G^{*}\), J/mm² | \(G^{*}/h\), J/mm³ |
|------------------------|-------|-----------|-----------------------------|--------------|--------------|--------|----------------|-------------------|
| Unfilled lacquer       | 0.123 | 260       | 7.6                         | 3.72         | 9.4          | 0.836*10⁻³ | 320.5           | 2605.3            |
| TiO₂-filled sample     | 0.112 | 270       | 7.8                         | 4.53         | 11.4         | 2.689*10⁻³ | 40.8            | 363.8             |
| ZnO-filled sample      | 0.098 | 250       | 7.7                         | 3.6          | 9.15         | 1.11*10⁻³ | 133.9           | 1366.1            |
| SiO₂-filled sample     | 0.216 | 246       | 6.8                         | 4.59         | 12.59        | 4.687*10⁻³ | 30.5            | 141.0             |

Scratch testing was performed on the mechanically unaffected coating surface, and hence the effect of additional processing on the obtained results was avoided. The testing temperature was 24±2 °C. Preloading was performed, the indenter being brought to the coating and loaded to 1 N). The indenter then moved with an increasing load. The combination of the normal load applied to the indenter and its tangential displacement induces complex stress and strain fields in the scratch region and, as a consequence, adhesive and cohesive failures of the coating. Herewith, the adhesive and cohesive failures are competing processes, able to develop both sequentially and in parallel [8]. In each case, the experiment was stopped at the moment of macrocracking in the coating material.
To estimate the adhesion energy, we made 3 scratches on each sample, with an indenter velocity of 0.001 mm/s. The table moved at a speed of 0.07 mm/s. After scratch testing, the coating surface relief was examined and quantitatively described by optical microscopy with an MBS-1 binocular stereoscopic microscope.

In this paper, the value of specific elastic energy per the unit area of the cohesion boundary, hereinafter referred to as adhesive failure, is used as to characterize adhesive failure through coating delamination from the substrate [9,10], which, in the absence of residual stresses in the coating, can be approximately determined as

$$G^* = Z \frac{\sigma^2 h}{E}$$

(1)

where $$h$$ – is coating thickness, $$E$$ – is Young’s modulus for the coating material, $$Z = 1$$ at the onset of delamination, $$\sigma$$ is the tangential component of the indenter pressure affecting coating during scratching at the onset of delamination, which is determined as

$$\sigma = \frac{F_t}{S}$$

(2)

where $$F_t$$ is the tangential component of the force affecting the coating during scratching, $$S$$ is the area of the vertical projection of the indenter–coating contact surface at the onset of delamination (figure 1).

3. Experiments, results, and discussion

The general view of the scratch length dependences of the normal force ($$F_N$$) and the lateral force ($$F_L$$) for different kinds of the coating material is depicted in figure 2,a and b, respectively. The local variations in the values of the normal and lateral forces recorded on the scratch diagrams (figure 2) are most likely associated with piling on the scratch bottom and sides, which is caused by indenter sliding, and with overcoming it. It is obvious from figure 2 that the highest lateral and normal forces to macroscopic failure are sustained by the coating filled with silicon dioxide and then titanium dioxide.

Figure 1. A cross section of scratch testing.

Figure 2. Scratch length dependences of the normal force ($$F_N$$) and the lateral force ($$F_L$$).
The unfilled epoxy lacquer withstands the lowest loads to failure. The values of hardness and the reduced modulus for the coatings under study are given in table 1. It was reported in [6] that, for the coating filled with titanium dioxide, the Martens hardness determined under steady-state indentation conditions increases by 4% from the unfilled coating, this being typical of this additive [2]. In turn, the introduction of zinc oxide and silicon dioxide reduces HM by 4 and 5.5%, respectively, although different results can be found in the literature. For the coatings filled with zinc oxide, the values of the contact elastic modulus remain on the level of the values for the unfilled epoxy lacquer, whereas they decrease by 9% for the coatings filled with silicon dioxide.

Having compared the data on the forces in scratch testing and the data on material hardness, one can conclude that the addition of silicon dioxide decreases the hardness of the coating slightly, but the sustained normal and lateral scratching forces increase by a factor of 5 and 4.4, respectively (see figure 2). For the coating doped with TiO₂, the normal and lateral scratching forces sustained prior to failure double in both cases. For ZnO, the sustained forces increase by a factor of 1.7, see figure 2.

The macrocracking in the coating material is preceded by adhesive failure, i.e., delamination of the coating from the substrate. The general view of cracking for a sample coated with the unmodified lacquer and for the coating filled with SiO₂ is exemplified in figure 3,a and b. It is obvious from figure 3,a that, for the unmodified lacquer, delamination (adhesive failure) occurs practically immediately after the start of scratching; a similar situation is observed for the coating modified with zinc oxide. In turn, for the lacquer with 10% of silicon dioxide, there is originally a portion of scratching without adhesive or cohesive failure. Table 1 shows the value of tangential $F_t$ and normal $F_p$ forces at which adhesive failure occurs and the values of the area of the vertical projection of the indenter–coating interface at the delamination onset, $S$. Herewith, coating delamination occurs at a depth smaller than the thickness of the coating proper. It can be concluded from the obtained data that the unfilled lacquer used as a coating is characterized by poor adhesion since coating material delamination from the substrate happens even under low applied loads, yet without failure of the coating proper, i.e., the failure is adhesive.

Formulas (1) and (2) are used to calculate the value of the surface energy of adhesive failure $G^*$. Since the coating thickness is different each time, we consider the specific value of the surface energy of adhesive failure per unit coating thickness $G^*/h$.

Adhesive energy is often used for a quantitative description of adhesive failure [11–13]; however, the problem on the unity and uniformity of a quantitative measure for the strength of an adhesive coating has yet to be solved completely [14]. As is seen from table 1, the values of $G^*$ differ greatly for different coatings, and it is impossible to relate uniquely the introduced additive to the adhesive failure energy of the coatings. The energy $G^*$, in its turn, depends on a number of parameters, which vary greatly for different fillers. By equation (1), we find some critical energy value indicating the limit which must not be exceeded when these coatings are to be deformed and which can be used in
predicting the behavior of the loaded coatings. Besides, the use of this parameter enables us to conclude about the fracture energy consumption of the coating. The most energy-consuming fracture occurs in the unfilled lacquer, the least energy-consuming fracture being characteristic of the SiO$_2$-filled sample.

4. Conclusion
It has been found that adhesive failure prevails for the studied systems and that further increasing loading causes cohesive failure of the coating material, with a subsequent combination of both failure mechanisms, thus eventually leading to coating chipping.

As compared with the unfilled coating, the introduction of the additives increases the sustained tangential and lateral forces during scratching to macrofracture and, therefore, increases the ability to withstand high operating loads. The greatest increase in the sustained forces (5 and 4.4 times, respectively) is observed for the silicon dioxide filler.

The study of energy has revealed that the failure of the unfilled lacquer is the most energy-consuming and that the least energy-consuming failure is demonstrated by the sample doped with SiO$_2$.

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