Progress in Organic Coatings 125 (2018) 325–330

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

A correlation between the Wolf-Wilburn scale and atomic force microscopy for anti-scratch resistance determination

Daniel Domene-López*, Juan Carlos García-Quesada, Ignacio Martín-Gullón

Chemical Engineering Department, University of Alicante, P.O. Box 99, Alicante, Spain

A R T I C L E I N F O

Keywords:
Coating
Pencil hardness
Wolf-Wilburn
AFM
Urethane-acrylate
Bar coating

A B S T R A C T

The quality of coatings is continuously improving due in part to the irruption of nanotechnology in material science, which has made it possible to manufacture novel nanocomposites. Similarly, the methodologies to measure the mechanical properties of polymer-based nanocomposite coatings are changing. However, a real standard to measure, for example, anti-scratch resistance using equipment such an Atomic Force Microscope (AFM), does not exist due to the strong influence of operational conditions on the final results. This means it is impossible to compare the results of different authors. Moreover, traditional methodologies used in industry, like the Wolf-Wilburn Test, are not able to measure the hardness of novel composites since they can go out of scale. In this work, an AFM is used to make nano-scratches in urethane-acrylate coating surfaces with known Wolf-Wilburn scale values, calculating the anti-scratch resistance. These data are correlated through linear regression. This correlation could be used to obtain the Wolf-Wilburn values from the width of groove made on the polymer surface by the AFM tip. Thus, this work present a potential way to extend the Wolf-Wilburn scale using AFM for those coatings that could not be measurable with Wolf-Wilburn Test.

1. Introduction

Polymeric coatings have a wide range of applications in daily objects (automobiles, facades, furniture, etc.). Coatings in the form of varnishes, lacquers or paint are frequent: approximately 40% of the coatings produced in the world are used for the decoration and protection of final products [1]. Apart from a any aesthetic purpose, coatings can be used to protect a surface against external chemical, mechanical, corrosive and environmental agents. In general, a coating is composed of a blend of polymeric resins, solvents and additives or pigments that modify its properties or aspect. Depending on the kind of resin or polymer used, two different types of coatings exist: thermoplastics and thermosets. While thermoplastic coatings contain at least one high molecular weight polymer responsible for part of the final properties of the coating, thermoset coatings involve the use of low molecular weight resins and monomers that polymerize under the effect of heat or radiation [2].

Manufactures are continuously developing new formulations for coatings for high performance applications (automotive, corrosion protection, marine application, etc.), with progressively enhanced properties. From the point of view of coating processing and characterization, hundreds of standards and tests have been developed, such as those from the ASTM or ISO standard organizations. Different properties can be studied in coatings, such as adhesion, resistance to abrasion, corrosion, biodegradation, weather, etc. Among them, hardness is the most important because it determines part of the protective ability of the coating.

Hardness (or normal hardness) is the resistance against plastic deformation [3] and is defined as the applied vertical load divided by the residual surface impression of a tip, generated after the application of a force. Normal hardness, as well as other parameters like the Young's Modulus, have been studied for many years by indentation [3,4]. However, indentation assays present several disadvantages such as the impossibility of obtaining direct measurements with indentation equipment and involve tedious methodologies, since additional techniques, such as Scanning Electron Microscope (SEM), are required for the observation and measurement of the marks produced on the surface by the indenter. Anti-scratch resistance, together with hardness, is another parameter used to characterize the final quality and performance of a coating [5].

Anti-scratch resistance can be easily measured with the Wolf-Wilburn method (W.W), which is described in ASTM Designation 3363-05 [6]. This is a common straightforward technique, mainly due to its low cost, and it is still been accepted in the coatings industry [7]. The method is based on the quantitative measurement of anti-scratch resistance by using pencils of different hardness and determining the one

* Corresponding author.
E-mail address: daniel.domene@ua.es (D. Domene-López).

https://doi.org/10.1016/j.porgcoat.2018.08.012
Received 16 April 2018; Received in revised form 21 June 2018; Accepted 6 August 2018

that can make a linear mark on the coating surface. This scale consists of two wide regions: B for soft pencils and H for hard pencils.

9B-8B-7B-6B-5B-4B-3B-2B-B—HB—F—H-2H-3H-4H-5H-6H-7H-8H-9H

Nevertheless, recent advances in nanotechnology have introduced nanocomposites in novel applications with higher performances, especially regarding hardness, whose values are beyond those measurable on the pencil scale. These samples, commonly polymers, are with inorganic particles with the objective to improve their mechanical properties [8–11].

At the same time, novel techniques to determine the mechanical properties of samples are continuously appearing in the materials science field. During the last decade, techniques based on nanoindentation or nano-scratching have been gaining importance. For example, using an indenter, Fereidoon et al. [12] investigated how the introduction of carbon nanotubes modified the hardness of a polystyrene composite. Suriano et al. [13] used zirconia-based sol gel to develop hybrid coating and studied improvements in anti-scratch hardness by AFM. Bobzin et al. [14] studied the plastic deformation of chromium-based nitride hard coatings using a nanoindenter and SEM. Jeng et al. [15] used AFM to determine the mechanical properties of a hydrogenated diamond like carbon coatings. Although the number of research works that use nanoindentation techniques is continuously increasing, it is difficult to compare results due to the influence of the sample material structure and operational conditions. For example, Csanádi et al. [16] studied the influence of the grain domain of a ZrB_2 ceramic on the hardness of the material measured by nanoindentation and AFM techniques; the hardness or scratch resistance can be measured by the permanent deformation provoked in a sample, so the depth or width of the penetration attained may offer information about this parameter. For example, Krupička et al. [17] used a section of the furrows created to build a generalized scratch map for a material, showing the different responses expected (elastic, ploughing, rupture, etc.) at different contact loads and rates. Kotsikova et al. [18] characterized polymer/graphene bilayer coatings using different indentation techniques and AFM, using the depth of the grooves of the samples to characterize the mechanical properties. Thus, from the point of view of materials characterization, it is crucial to understand the interrelationship between the macro-properties measured with an industrial technique such as the Wolf-Wilburn procedure, and nano-scratch properties measured with a technique like AFM. Similar studies exist in the literature; for example, when a property as the Mohs scale was successfully correlated with indentation measurements [19], while Kim et al. [7] determined the normal hardness by indentation of different pencils and presented a correlation.

The aim of the present work was to study the anti-scratch resistance of different coatings using two different procedures: nano-scratching by AFM and Wolf-Wilburn Test. The results are compared and a clear correlation between both techniques is established. Following the methodology presented in this paper, this will allow to the results obtained by both techniques (in terms of a common scale) to be compared with other research works, and to determine anti-scratch resistance beyond Wolf-Wilburn standard. This correlation could permit the extrapolation of AFM results to regions off the Wolf Wilburn scale in terms of conventional pencils. It could also permit the determination of anti-scratch resistance in terms of the Wolf-Wilburn scale for extremely hard coatings where graphite pencils are of no use.

2. Materials and methods

2.1. Preparation of samples

A commercial formulation high performance anti-scratch coating was chosen based on a urethane-acrylate thermoset resin with a rapid UV curing process at room temperature [20,21]. The resin system is composed of a urethane-acrylate oligomer (Laromer UA9048) and

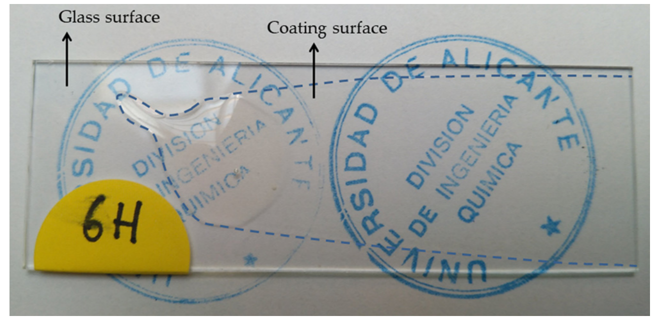

Fig. 1. Coating with a hardness value of 6H.

Table 1
Wolf-Wilburn hardness (H_w) for the samples prepared, keeping constant the proportion of Laromer UA 9048 and Laromer LR 8887 (4:1) and varying the reaction time and photo-catalyst concentration.

Reaction time (min)	Photo-catalyst concentration (%)							
	3	3.5	4	4.5	5	5.5	6	7
0.5	< HB	< HB	HB	2H	5H	6H	5H	6H
2	2H	3H	6H	6H	6H	8H	6H	6H
5	6H	6H	7H	6H	7H	8H	8H	6H
10	6H	7H	7H	6H	7H	8H	8H	8H
15	7H	7H	8H	8H	8H	8H	8H	8H
20	7H	7H	8H	8H	8H	8H	8H	8H

trimethylolpropane formal acrylate (Laromer LR8887) as a thinner (kindly supplied by BASF, Schwarzheide GmbH, Germany) using four parts of oligomer per part of thinner. 2-Hydroxy-2-metylpropiophenone [which presents a maximum of absorbance at a wavelength of 250 nm] from Sigma Aldrich (Madrid, Spain) was used as photo-catalyst.

Different coating formulations were prepared mixing the three main components, under magnetic stirring and avoiding any type of light, which could initiate premature polymerization. Once the formulation was homogeneous (after 5 min), a drop of mixture was poured onto a glass surface. The mixture was spread with the help of a coating bar (Printcoat instruments Kred model, Litlington, England), obtaining a 12 μm thickness film, which was put into a UV-chamber. The UV-chamber consisted in a cylindrical chamber covered with aluminum foil and provided with a 55 W Ultraviolet type C (UVC) mercury lamp.

Different formulations were prepared at different initiator concentrations (3, 3.5, 4, 4.5, 5, 5.5, 6 and 7%) and curing times (0.5, 2, 5, 10, 15 and 20 min) since these are the most determinant factors in the mechanical properties of the final coating.

2.2. Wolf-Wilburn test

A set of draw pencils (Derwent Graphics, England), with a well-known hardness value on the Wolf-Wilburn scale (H_w) was used. The ASTM Standard 3363-05 [6] describes the test, which consists of determining the pencil with the maximum hardness that cannot produce a mark on the surface of the coating. The hardness value of the pencil is the anti-scratch resistance of the coating.

2.3. Nano-scratch measurements with the atomic force microscope

An Atomic Force Microscope (NT-MDT NTEGRA PRIMA model) was used to make nano-scratches on the surface of the coatings. In conventional indentation tests, hardness is defined as follows [3,4,22]:

$$Hardness = F_a/A_c \quad (1)$$

where F_a is the normal load and A_c is the residual surface impression of the mark after application of the force. To determine anti-scratch