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Film formation analysis by diffusive wave spectroscopy

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A B S T R A C T

The thin layer analysis is very important for several sectors of industry. Indeed, environmental laws and improvement of performances lead the manufacturers to innovate in the field of coatings and paints. Several classical techniques of characterization (TGA, DMA, etc.) used with this intention do not allow to perform the analysis in situ and are often long and tedious to set up. We propose to solve this problem with a new optical process. Its technology based on multi-speckle diffusive wave spectroscopy (MS-DWS) allows making real-time analysis in a non-destructive way thanks to an optical measurement. The aim of this work is to highlight correlations between this new technology and the classical methods of analysis. Two film forming polymeric materials were studied, a polydimethylsiloxane (PDMS) and a commercial paint based on an aqueous dispersion of acrylic copolymers. The PDMS was chosen for the simplicity of its film forming process and is used as model. The paint having a more complex drying mechanism enables to complete this study.

Keywords:

MS-DWS
PDMS cross linkage
Latex film formation

1. Introduction

Paints and coatings are currently an important field in aeronautics, car or construction industry. The new environmental legislations involve a constant research in new coatings which are more environmentally friendly. In order to make sure that these new coatings have the same properties, it is necessary to carry out analyses to understand the mechanisms involved during the film formation. Different standard techniques of analysis, such as thermogravimetric analysis (TGA) or dynamical mechanical analysis (DMA) are usually used. However, these techniques do not allow to study the coatings under real conditions of use.

The aim of this work is to investigate film formation thanks to an optical technique. Studies on thin layers of coatings were already carried out through optical methods, such as infrared spectroscopic ellipsometry (IRSE) [1] and speckle interferometry [2,3]. In this study, the instrument used is based on the principle of the multi-speckle diffusive wave spectroscopy (MS-DWS). It is a non-invasive technique, which enables to analyse the film formation by determining a drying time and giving information on the physicochemical phenomena which occur during the formation of film. However, a correlative study between the MS-DWS and classical techniques of characterization, such as thermogravimetric analysis (TGA), Fourier transform infrared

spectroscopy (FT-IR) and dynamical mechanical analysis is necessary to better understand the film forming process. To carry out this study two polymers were chosen. First a polydimethylsiloxane (PDMS) used as model and then a water-based paint containing acrylic copolymers. The paint having a more complex drying mechanism enables to look at real industrial formulations.

2. Experimental

2.1. Materials

2.1.1. Polydimethylsiloxane

The polydimethylsiloxane is a three-dimensional elastomer where the principal chain is made from Si-O bonds. The PDMS used was provided by Rhodia. This PDMS is a monocomponent cross linking at room temperature in the presence of moisture. It is translucent, without solvent with an acetic odour. In order to have some backscattering signal, 15% (w/w) of polytetrafluoroethylene particles (PTFE) are added to the PDMS. The PTFE particles provided by Clariant are given with a diameter of 5.5–10.5 μm .

2.1.2. Acrylic polymer paint

The commercial paint used, provided by Tollens, is a dispersion of latex particles (acrylic polymer). The main solvent is water. The drying mechanism of this paint is happening in several steps and described extensively in a previous publication [4].

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2.2. Methods

In both cases, the samples are coated on an aluminium substrate. The composition and the thickness are monitored. All the measurements are made in atmospheric laboratory condition and at controlled ambient temperature.

2.2.1. Multi-speckle diffusive wave spectroscopy

A new method based on the diffusive wave spectroscopy and named A.S.I.I. (Adaptive Speckle Imaging Interferometry) was used to analyse the film formation process [5]. The instrument is named Horus[®] and manufactured by Formulaction (France). The principle of measurement consists in sending a laser light (630 nm) into the film. A part of the light is backscattered by the scattering materials (emulsion droplets, latex particles, fibers, etc.) present in the sample and detected by a video camera through an interference image, also called speckle image. In the case of a film forming sample, the motion of the scatterers slows down and the deformation speed of the speckle pattern, or speckle rate, decreases as the sample dries. By monitoring the speckle rate during film forming process structural changes in the drying coating sample can be observed. The technique enables to work on any kind of substrate with the required thickness in realistic conditions.

For this study, the samples are drawn on an aluminium plate with a wet thickness of 250 μm for the PDMS and 120 μm for the paint.

2.2.2. Thermogravimetric analysis

The thermogravimetric analysis is performed in a TA Q50 (TA Instruments). It consists in measuring the variations of mass according to time at constant temperature. For the PDMS, samples of about 5 mg are maintained at 25 $^{\circ}\text{C}$ during 2 h. For the paint, samples are about 13 mg weight and the temperature is also held at 25 $^{\circ}\text{C}$ but for 3 h. Both products are deposited in an aluminium pan. The thickness of the samples is measured dry. As PDMS cross link with water, the thermogravimetric analyser is equipped with a gas washing bottle to humidify the gas flow [6].

2.2.3. Fourier transform infrared spectroscopy

The Fourier transform infrared spectroscopy enables to follow the polymerisation of PDMS at the chemical level. The measurements are performed in a FT-IR BX spectrometer (from PerkinElmer) in transmission mode. The PDMS is spread on a KBr disc and the spectra are acquired at fixed time space. The measurement settings are four scans with a resolution of 2 cm^{-1} from 4000 to 1000 cm^{-1} .

2.2.4. Dynamic mechanical analysis

The rheological analysis consists in looking at the evolution of the viscoelastic behaviour of the sample according to time. In order to be as close as possible from realistic conditions, the sample is spread on the two faces of an aluminium foil and the whole is disposed between two jaws. The dynamic mechanical measurements are performed in the ARES (Advanced Rheometrics Expansion System, from TA Instruments). The geometry of the measurement is a rectangular torsion. To obtain only the PDMS response and to fix the measurement parameters, a deformation scan of the aluminium foil is realized. Hence the elastic area of the aluminium is determined. The foil is 5 cm long and 1 cm wide. The angular speed is 1 rad s^{-1} , the deformation 0.001% and the axial strength 100 g in traction. The shear modulus G' is plotted as a function of time.

2.2.5. Characteristic times

The Horus[®] instrument giving kinetics, all the values measured by the other methods will be given according to time and in order

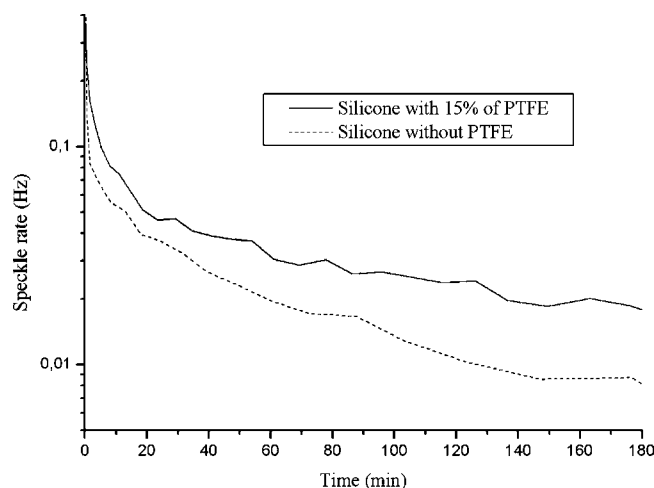


Fig. 1. Comparison of drying kinetics between PDMS with and without PTFE particles by diffusive wave spectroscopy.

to compare these results, the experimental conditions are given according to those used during Horus[®] measurements. All the characteristic times are measured in the same way. They are determined by the intersection of the tangent situated at both extremities of the phenomenon.

3. Results

3.1. A model behaviour: one characteristic time system

To make sure that the PTFE particles added in the PDMS are inert, measurements on Horus[®] are performed with and without PTFE. Fig. 1 shows similar curves, confirming the small effect of the particles in the system regarding film formation. The difference in speckle rate observed is due to the amount of scatterers: the more scatterers, the higher the speckle rate. Considering this result, the PDMS contains 15% (w/w) of PTFE for every measurement to ensure good optical properties. Several trials were performed to confirm the good reproducibility (data not shown).

Fig. 2 the evolution of the speckle rate for a PDMS film is plotted. It shows that the speckle rate decreases and tends to a plateau. The characteristic time extracted is about 8 min and the dry thickness is 130 μm . Fig. 3, the same system is monitored via TGA. The weight

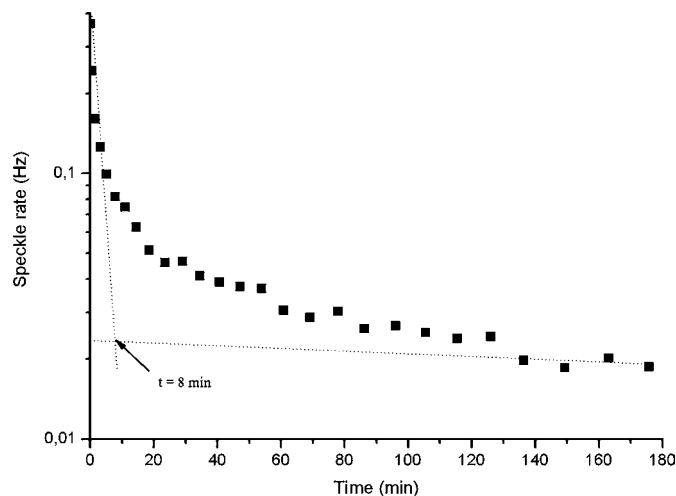


Fig. 2. Drying kinetics of the PDMS by diffusive wave spectroscopy.

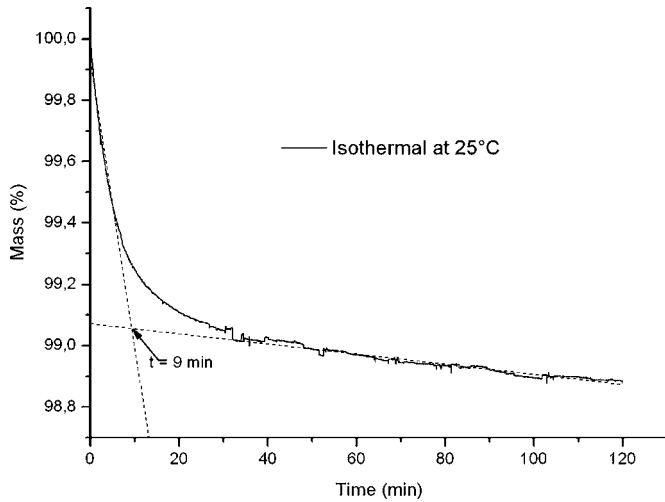


Fig. 3. Isothermal of the PDMS at 25°C.

loss observed is weak ($\approx 1\%$), showing first a quick decrease and a stabilization. The dry sample is $140\ \mu\text{m}$ thick and the characteristic time is about 9 min, which is very close to the Horus[®] one. The IR spectra at different times are overlaid in Fig. 4. Some peaks vary according to time, especially the one situated at almost $1743\ \text{cm}^{-1}$. This peak decreases gradually until disappearing. By plotting the transmission of this peak as a function of time, it is possible to obtain a kinetic of the PDMS polymerisation (Fig. 5). The transmission increases until reaching a plateau. The characteristic time extracted is 12 min.

The rheological analysis consists in measuring the shear modulus G' as a function of time. By being in the linear area of the aluminium foil, the variation of G' is representative of the PDMS behaviour. According to Fig. 6, the shear modulus increases until reaching a plateau. The characteristic time is about 10 min.

3.2. A complex behaviour: multiple characteristic time system

In this part a fully formulated paint is studied, showing the complex behaviour of industrial products. In thermogravimetric analysis (Fig. 7) the weight loss is about 31%. The curve decreases

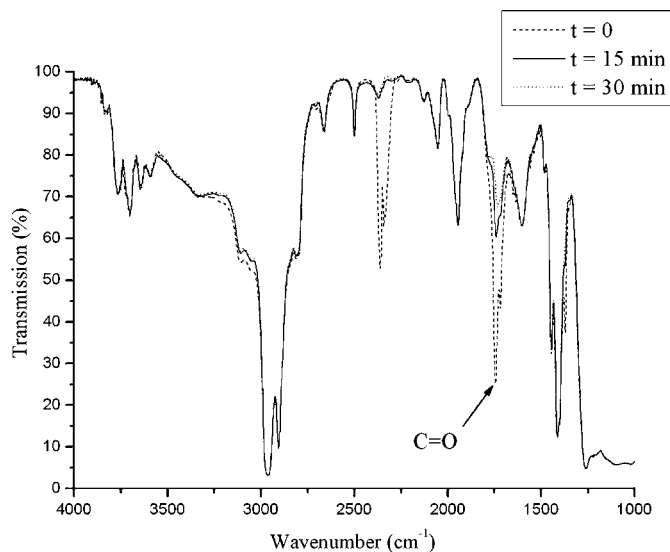


Fig. 4. IR spectra of the PDMS at 0, 15 and 30 min.

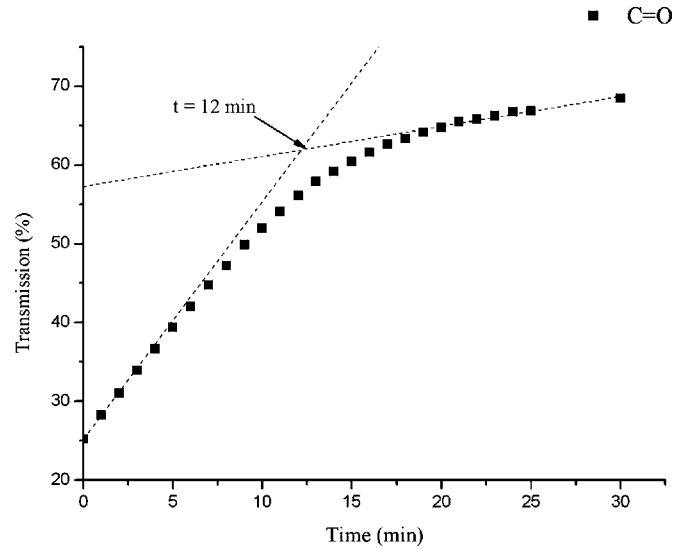


Fig. 5. Transmission as a function of time for the C=O peak.

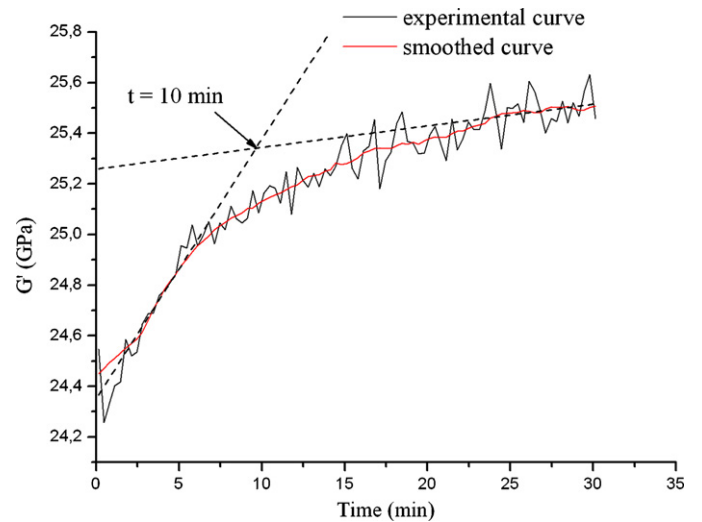


Fig. 6. Shear modulus as a function of time of the PDMS.

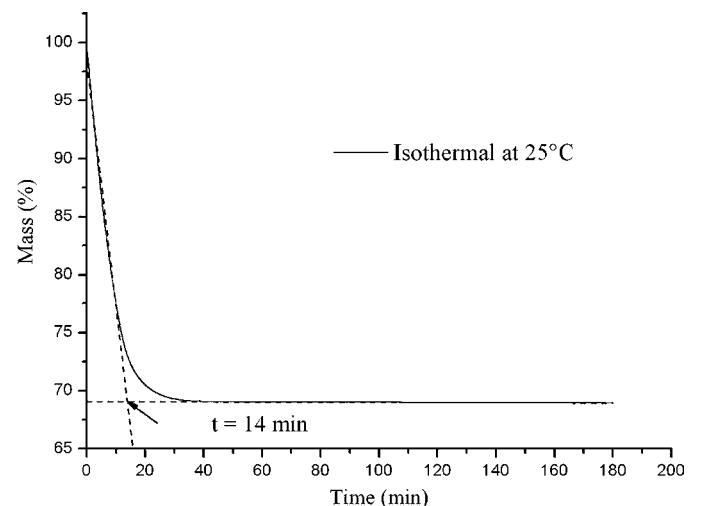


Fig. 7. Isothermal of the paint at 25°C.

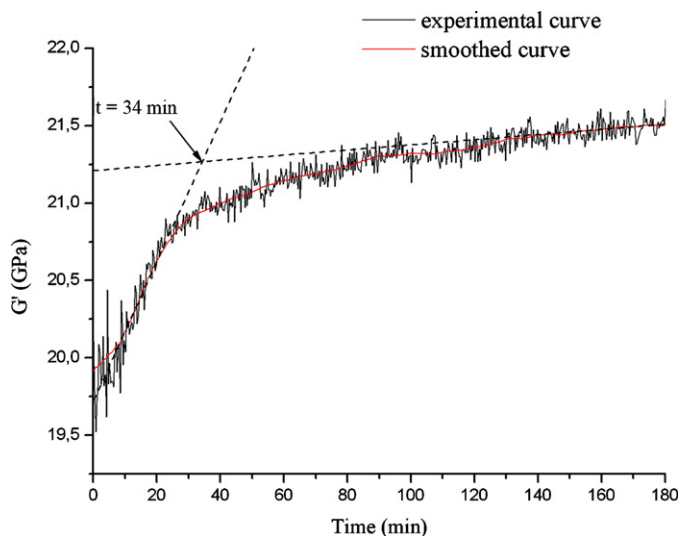


Fig. 8. Shear modulus as a function of time of the paint.

sharply to tend to a plateau. The characteristic time is about 14 min and the dry thickness around $60\ \mu\text{m}$. The rheological analysis (Fig. 8) is performed in the same conditions as for the PDMS. G' increases until reaching a plateau. The dry sample is $200\ \mu\text{m}$ thick and the characteristic time is 34 min. With MS-DWS experiments, the sample layer is $120\ \mu\text{m}$ wet thick, which corresponds to $60\ \mu\text{m}$ dry. As shown in Fig. 9, the curve obtained MS-DWS can be divided into three parts. First the speckle rate decreases slightly up to 9 min. In the second part the signal is agitated, showing quick increases and decreases. Then it decreases again sharply to end up being constant with a characteristic time of 35 min.

4. Discussion

4.1. A model behaviour

The decrease observed in MS-DWS (Fig. 2) is explained by the cross linkage itself. At the beginning the chains are weakly reticulated and the scatterers can easily move so the speckle rate is high. When the three-dimensional network develops, the scatterers are obstructed and the speckle rate decreases. The plateau corresponds to the end of the cross linkage when the film is formed.

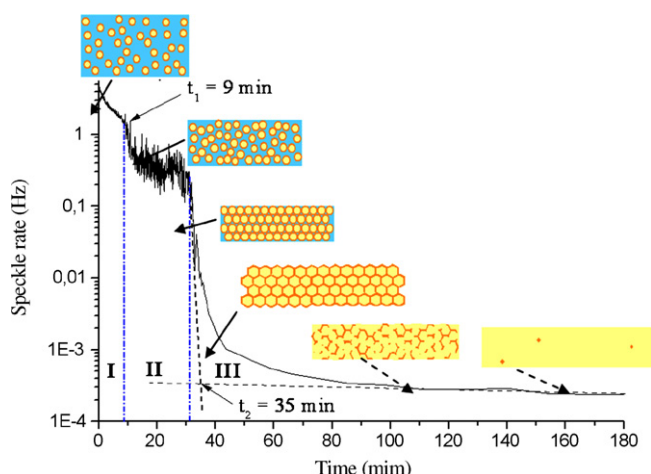


Fig. 9. Drying kinetics of the paint by diffusive wave spectroscopy.

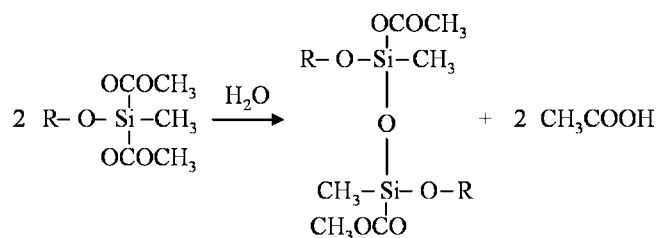


Fig. 10. Cross linkage mechanism of the PDMS.

The weak weight loss observed in TGA (Fig. 3) can be explained by the absence of solvent, only the by-products of the cross linkage are emanated. This result is characteristic of the PDMS cross linkage. Indeed, at the beginning of the reaction the by-products are not obstructed by the weakly reticulated chains. As soon as the three-dimensional network develops, the reactive terminations of the chains are imprisoned, and the reaction is slowed down. The IR analysis enables to follow the kinetics of the PDMS cross linkage. The peak observed at $1743\ \text{cm}^{-1}$ in Fig. 4 corresponds to the $\text{C}=\text{O}$ bond of a carboxylic acid. During reticulation, acid groups are released as seen in Fig. 10 [7,8], which explains the curve obtained in Fig. 5. The plateau corresponds to the disappearance of carbonyl groups and so to the end of the cross linkage. The characteristic time is longer than in speckle interferometry. It is probably due to the colder temperature during the FT-IT analysis, which cannot be controlled at the time of the measurements, slowing down, the kinetics of the PDMS cross linkage. In rheological analysis, the physical state of the PDMS evolves when the three-dimensional network is forming. That explains the increase of the shear modulus G' observed in Fig. 6. G' grows up until the cross linkage is over. The small difference with the MS-DWS time can be explained by the thickness of the dry coat ($230\ \mu\text{m}$ thick for rheology, against $130\ \mu\text{m}$ for MS-DWS). Indeed, to obtain a significant signal in rheology, the sample must be thicker than the other methods. The PDMS is a simple case to study. The only one phenomenon taking place is the cross linkage and so the results are easily comparable. All different characteristic times are of the same order of magnitude. The kinetics obtained in MS-DWS on the PDMS in a good agreement with the curing phenomenon.

4.2. A complex behaviour

The thermogravimetric analysis of the acrylic commercial paint enables to highlight only one phenomenon as can be seen in Fig. 7. The 31% weight loss corresponds to the solvent evaporation. There is also only one phenomenon observed in DMA (Fig. 8). During the film forming process, the shear modulus directly connected to the viscosity, increases. When the plateau is reached the film is formed. The curve obtained in MS-DWS (Fig. 9) matches with the three stages typical of water-based systems [9]. The stage I corresponds to a concentration of the environment due to the evaporation of the solvent. When the concentration is sufficiently high, the particles get closer to each other, collide which leads to accelerations and decelerations of the particles and explains the variations observed in the stage II. When the scatterers are closely packed, their motion decreases strongly (stage III of the curve). This stage corresponds to the film strengthening by elimination of the interstitial solvent and eventually by phenomena of interdiffusion of the latex particles. By comparing the results obtained by different methods, some correlations can be established. The time in TGA and t_1 in MS-DWS both correspond to the evaporation. However the TGA time (14 min) is longer than t_1 (9 min). That means that the evaporation phenomenon observed in MS-DWS happens in the stage I but also

continues in stage II. The time t_2 in MS-DWS (35 min) is close to the one in rheology (34 min). The phenomenon observed in DMA seems to correspond to the whole drying mechanism. Nevertheless the different thicknesses do not allow us to assert.

5. Conclusion

This study allows to establish some correlations between MS-DWS and the classical techniques of characterization used for coatings. For the PDMS, which is a model material, the phenomenon observed in MS-DWS can be identified as being the PDMS cross linkage. The paint is a more complex material. The A.S.I.I. technology enables to determine the three stages corresponding to the characteristic drying mechanism of this kind of paint, but those stages are not all highlighted by the traditional methods. However, the TGA allows fixing the evaporation in the stage I but also in a part of the stage II. The time t_2 in MS-DWS being very close to the one in rheology, the phenomenon observed could correspond to the whole drying mechanism. In conclusion, this new A.S.I.I. tech-

nology enables to determine drying times in an objective way but also to observe and characterize the phenomena occurring during the film formation in a non-destructive way and under simple and representative conditions.

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