Analysing Organic Coatings

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Abstract

Apart from routine mechanical testing of organic coatings, analytical methods such as FTIR, differential scanning calorimetry (DSC) and instrumented indentation test can be used to provide useful, complementary information about a coating's final properties, which are determined by how well it has been cured. These methods are relatively simple, and yet practical for application in the coatings industry.

Introduction

The properties of a thermosetting coating system is significantly determined by how well it has been cured (crosslinked). A coating that has been properly cured will be able to achieve its targeted properties, as well as the performance it has been engineered for. The reverse is true if the coating has been undercured or overcured. The curing process is therefore a very important step in any coating application, and as such it requires relevant testing methods to ascertain whether this step has been done properly. In the industry, mechanical tests are widely used, such as pencil hardness, bending, cupping deformation, impact resistance, as well as solvent resistance tests.

While the mechanical testing of coatings are necessarily the norm and are cost-effective ways to ensure that the expected qualities are achieved, the use of analytical testing methods are arguably still relatively lacking in the Malaysian coatings industry particularly among the smaller manufacturers. This may be largely due to the higher cost of investing in the analytical instruments, as well as the cost to properly operate and maintain them.

It goes without saying that the industry cannot dispense with the mechanical tests. However, the adoption of analytical techniques should be given due consideration as they are in fact very useful and they complement the usual tests very well. There are of course many analytical techniques available and it is neither practical nor sensible to employ a host of these in routine applications. It is more reasonable to select a few that suit the needs of both the manufacturer and the end user. This article will briefly highlight some of the more useful and practical methods in the analysis of coatings, particularly in relation to the study of the relative degree of curing.

Results and discussion

Fourier Transform Infra-Red Spectrometry (FTIR)

FTIR, or more specifically the Attenuated Total Reflection (ATR)-FTIR method, is one of the most useful and accessible of all analytical methods for coatings. In fact the uses of FTIR and ATR-FTIR in the fingerprinting of wet paint have been described recently in the context of the Malaysian oil and gas industry [1-4]. The same method can be similarly adapted for cured coatings.

Among many others, one of the uses of ATR-FTIR analysis on coatings is the determination of the relative degree of curing. Figure 1 shows an example of this application in practice for a polyester-melamine coil coating system. The spectra show the changes on the band at about 910 cm^{-1} attributed to the methoxy groups of the melamine crosslinker present in the polyester coating cured at different peak metal temperatures (PMT). The 910 cm^{-1} band gets increasingly smaller with higher PMT as the crosslinking reaction between the melamine and the hydroxyl groups of the polyester resin results in the removal of increasing numbers of methoxy groups as methanol. The relative degree of curing can therefore be inferred from the comparison of the height or the areas under the band, where in this case the smaller areas would indicate a higher degree of crosslinking. This study can therefore provide useful information about how well a coating has been cured and should also be one of the first techniques used when troubleshooting a defective coating.

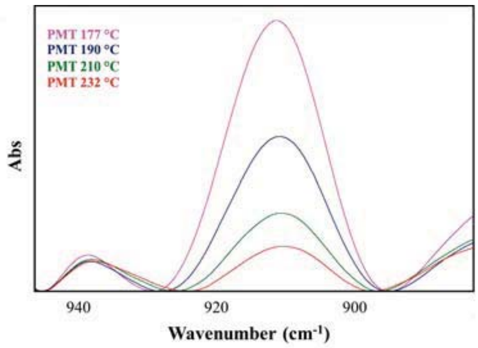

Figure 1 ATR-FTIR spectra of a polyester-melamine coating cured at different peak metal temperatures (PMT)

In order to apply this method for other coating systems, it is necessary to know whether the crosslinking reaction results in the increase or decrease in absorbance of any particular band when compared against an uncured coating. Provided that this band is not interfered with by other bands in the same region, i.e. these latter bands do not themselves change in absorbance at different extents of crosslinking, the selected band can therefore be used to observe the relative degree of curing of the coating. As a complement to the fingerprinting of a finished coating, the analysis of the selected band can be a useful tool to further ensure that the coating has been cured to within specifications.

Differential scanning calorimetry (DSC)

DSC is a thermal analysis technique commonly used to determine parameters such as glass transition temperatures (Tg), melting points and heat capacities of materials [5-8]. For coatings, the measurement of Tg is one of the most useful and essential techniques available. Tg is the temperature at which an amorphous material will transition from being in a glassy, brittle state into a soft, rubbery state. In other words, above the Tg, the material will behave very differently compared to its state when below the Tg.

Figure 2 shows the increase in the Tg of a polyester-melamine coating as its curing PMT increases. For this system, the coating appears to have approached an adequate degree of curing at a PMT of about 199-210°C where the Tg no longer appears to be increasing significantly. Knowing the Tg that a coating should achieve when properly cured is useful because this is the Tg at which the coating should achieve its specified properties and should therefore perform as expected.

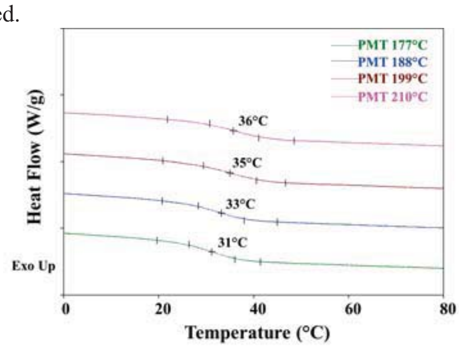

Figure 2 Stacked DSC thermograms showing the Tg (midpoint) of a polyester-melamine coating cured at different PMT

If the measured Tg of a coating is lower than expected, then it is usually undercured due to inadequate crosslinking and the coating will be relatively softer with a corresponding poorer performance in areas such as chemical resistance and dirt pickup resistance. An improved flexibility is usually observed but while this is normally desired due to a lower tendency for cracking, the overall poorer properties will result in the premature failure of the coating. Conversely, an overcured coating with excessive crosslinking will show a higher Tg than expected. The result is a coating which is more brittle and therefore more susceptible to cracking upon deformation or impact which can also lead to premature failure.

Instrumented indentation test

Instrumented indentation test, or microhardness, is a relatively lesser known technique in the analysis of organic coatings; the standards available today have only been around for the last decade or so [9-10]. It is different from the usual mechanical tests for hardness (such as pencil hardness) in the sense that this a non-destructive technique which is able to give information about the visco-elastic properties of a coating without the influence of the substrate, provided that the coating has adequate thickness.

The method uses a conventional Vickers indenter head to apply an ultra-low load on the coating. As shown in Figure 3, the test load is first increased gradually while the corresponding indentation depth of the measuring head is obtained. A holding cycle where the indentation is allowed to continue (creep) at a constant maximum load can be incorporated. The load is then gradually released to zero, while the coating relaxation displacement is measured. The hardness (Martens, HM or Universal, HU) is then calculated as the quotient of the applied load over the surface area of the resulting indentation. The indentation surface area is itself derived from the measurement of the indentation depth displacement and the well-defined geometry of the Vickers indenter.

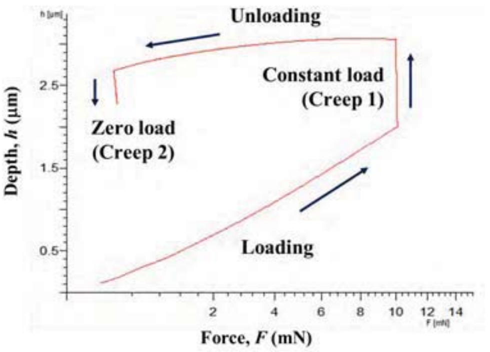

Figure 3 An instrumented indentation test profile showing the steps of increasing load, constant load, decreasing load, and zero load

The instrumented indentation test is usually carried out for a few times on the same sample and an average is obtained as the result. As the properties of organic coatings are also affected by temperature and humidity, it is also necessary to carry out the test under reasonably controlled conditions in order to have reliable comparative data.

Two of the more commonly used data that can be obtained from the instrumented indentation test include Martens hardness (HM) and indentation creep (C_{IT}). Table 1 shows the data for the same polyester-melamine coating cured under different PMT. HM can be seen to increase with PMT while at the same time C_{IT} decreases. This can be interpreted as an increase in the relative degree of crosslinking as PMT increases, which results in the increase in hardness and in a corresponding decrease in indentation creep. The properties at PMT 199°C and 210°C are not widely different, and they suggest that the coating has probably approached an adequate level of crosslinking at these temperatures, supporting the findings from the Tg analysis. As the results are obtained from the average of several measurements, a statistical comparison can of course be performed between the samples if so desired.

Table 1 Changes in Martens hardness and indentation creep with PMT as measured in an instrumented indentation test. Results are averaged from 9 measurements

PMT °C	HM (σ) N/mm^2	C_{IT} (σ) %
177	101 (13)	44 (5)
188	140 (9)	32 (2)
199	187 (19)	22 (2)
210	204 (19)	19 (1)

Conclusion

All the three techniques discussed in this article can be used to analyse the relative degree of curing of a coating, complementing the standard mechanical tests carried out routinely. Results from these analyses can be compared against data from tests such as pencil hardness, cupping deformation, impact resistance and even solvent resistance tests. While not shown here, good correlation can be observed between the analyses and the standard tests, for instance a coating with a relatively higher degree of curing will show better solvent resistance or scratch resistance, in correspondence with higher Tg. Having some analytical evidence on hand to explain the observations from standard tests can therefore be helpful. These techniques become even more indispensable when there is coating failure and the causes need to be understood. When used together, all three methods complement each other very well and are an especially strong combination in the curing study of a coating.

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HIGHLIGHTS

- Ms. Losini of MMU, won 3rd place in Young Persons' World Lecture Competition (YPWLC2014) in California, USA
- IMM nominated as Secretariat of AWF for 2 years

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