Analysis of the Rheological Properties of an Adulterated Two Component Epoxy Adhesive

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ABSTRACT

The aim of this work is to analyze an adulterated epoxy adhesive, sent off the market due to poor application conditions. This sample was compared with another one of reliable performance. The results of these studies revealed differences in the G* values between both adhesives, explaining the unsatisfactory behaviour of the adulterated sample.

INTRODUCTION

Adhesives and sealants require a complex array of rheological testing in order to characterize them and control the quality for end user satisfaction. Epoxies adhesives needs to flow easily during the mixing process of component A with component B, but they also need a quick recovery to finally adopt a solid consistency during the curing reaction.

Rheological measurements have become significantly important in the analysis of structural fluids, including quality control, storage stability under various weather and transportation conditions, effects of formulation on consistency, prediction of flow behaviour under manufacturing or environmental conditions[1].

In this paper we analyze the performance of an epoxy adhesive, sent off the market due to poor application conditions. The two components were compared with reliable ones. Amplitude sweep was measured for the yield point determination, frequency sweep for the time behavior, and a three interval test for recovery time. A chemical analysis was performed to look into the adhesive formulae.

EXPERIMENTAL

The samples were identified as follows: component A adulterated (A PROBLEM), component B adulterated **(**B PROBLEM), component A reliable (A RELIABLE) and component B reliable **(**B RELIABLE).

<u>Rheological behaviour</u>

The rheological behaviour was determined with an Anton-Paar Physica MCR301 Rheometer. The values of the storage modulus (G') and loss modulus (G'') were obtained in each test; and also the value of complex viscosity (η*) for the frequency sweep test.

An amplitude sweep test was made for the yield point determination, using the 50 mm cone-plate geometry at 10 1/s constant frequency and 0.1 to 100% range of amplitude.

A frequency sweep test was made for the time behaviour using the 50 mm cone-plate geometry at 0.1% constant amplitude and 0.1 to 100% range of frequency.

A three interval test (3ITT) was made for the recovery time, using the 25 mm parallel plate at 10 1/s constant frequency, 0.1% amplitude for the baseline and the structural regeneration interval, and 10% for the structural decomposition interval (outside the LVE range).

Chemical analysis

For the chemical analysis an IR Nicolet iS10 Infrared Spectrophotometer was employed with a Smart OMNI-Transmission Accessory. Components A, in both samples, were previously submitted to an 8 hours acetone extraction[2], the amount of which were informed as acetone extract (g/100 g). On the other hand components B, in both samples, were submitted to an 8 hours alcoholic extraction and informed as alcoholic extract (g/100 g).

An ash residual analysis was made in order to quantify the inorganic portion of the four samples[3]. These values were informed as ash residue (g/100 g).

RESULTS AND DISCUSSION

Rheological behaviour

In the amplitude sweep test, A RELIABLE presents a yield point at 135 Pa of Shear Stress (see Fig. 1). Meanwhile A PROBLEM presents a viscoelastic liquid behaviour during the entire measurement (no Yield Point).

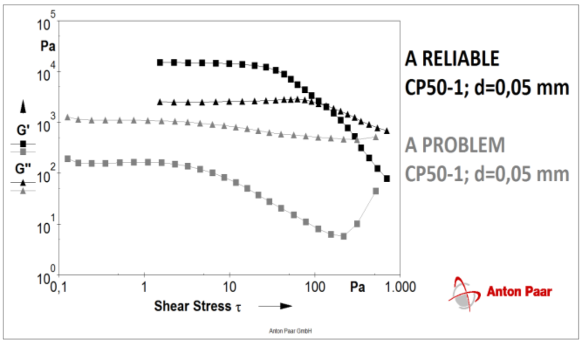

Figure 1. Amplitude sweep of components A for the Yield Point determination.

Similar behaviour appears in the components B measurement. With a yield point at 114 Pa for B RELIABLE and viscoelastic liquid behaviour for B PROBLEM (see Fig. 2)

The lack of Yield Point value for A PROBLEM and B PROBLEM could mean an unsatisfactory development during the application process due to an excessive amount of adhesive coming out the package with low effort[4].

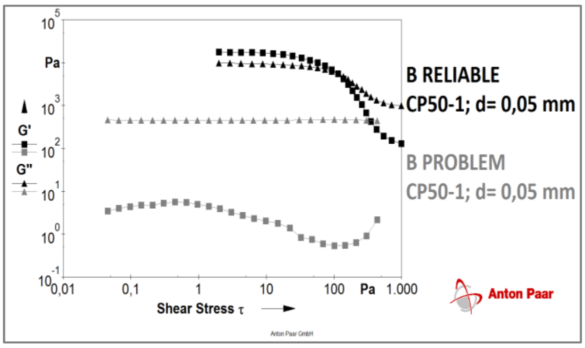

Figure 2. Amplitude sweep of components B for the Yield Point determination.

The frequency sweep test shows that A RELIABLE presents the ideal behaviour for epoxies adhesives: viscoelastic solid at low frequencies and viscoelastic liquid over 100 1/s of angular frequency. The A PROBLEM curves shows G'' over G' even at very low frequencies (see Fig. 3). The viscoelastic liquid consistency at rest leads to structural problems after the mixing and application process, such as sagging.

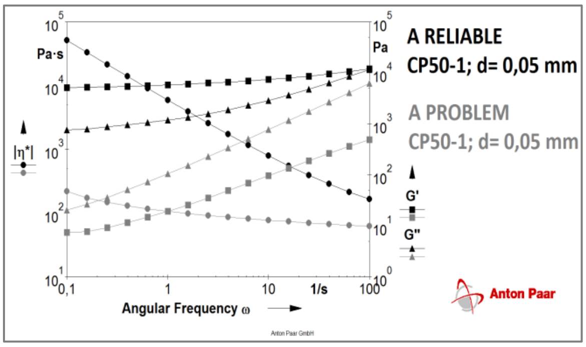

Figure 3. Frequency sweep of components A for the time behaviour determination.

B RELIABLE presents the predictable performance. The viscosity decreases and the material flow at high frequencies (over

10 1/s), but it has enough structure to be a solid at rest (see Fig. 4). B PROBLEM has a completely different structure; the constant viscosity indicates a Newtonian fluid behaviour and G’’ over G’ at low frequencies would lead to the same sagging problem than in A PROBLEM.

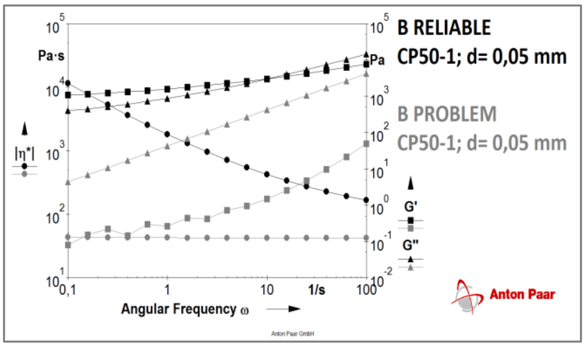

Figure 4. Frequency sweep of components B for the time behaviour determination.

The thixotropy test shows that once A RELIABLE is outside the LVE range, the material flows properly (see Fig. 5). But, when the measurement starts with the regeneration interval the sample adopt the solid structure instantly; and an almost full regeneration after 15 minutes analysis (see Table 1). A PROBLEM behaves as a viscoelastic liquid during the entire measurement but most important, during the regeneration interval, showing same complications as those detected during the frequency sweep test[5].

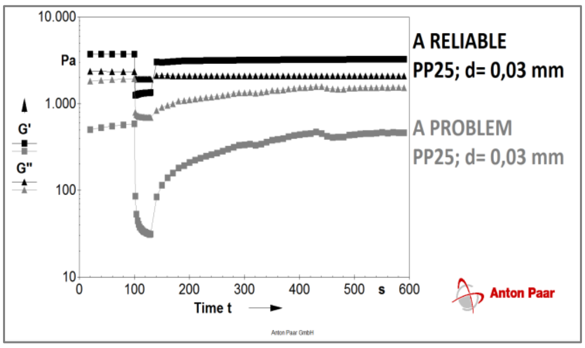

Figure 5. 3ITT of components A for the time recovery behaviour.

Table 1. Recovery ratio of components A during the thixotropy test.

Sample	G’ Baseline	G’ Regeneration	Recovery Ratio
A RELIABLE	3.74E+3	3.36E+3	0.90
A PROBLEM	5.88E+2	4.37E+2	0.74

B RELIABLE present similar behaviour than A RELIABLE during the thixotropy test (see Fig. 6). With instant regeneration at the third interval but only 50% recovery after 15 minutes analysis (see Table 2).

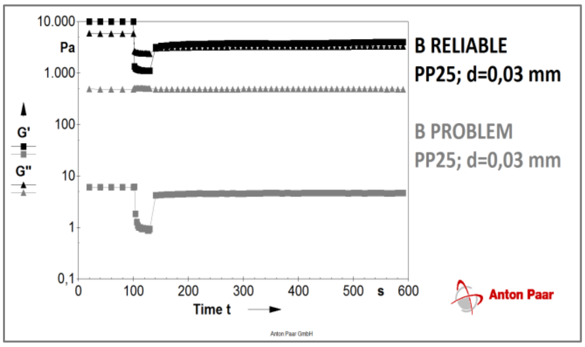

Figure 6. 3ITT of components B for the time recovery behaviour.

Although B PROBLEM has an acceptable recovery ratio, G’’ is higher than G’ during the entire measurement, presenting an inappropriate thixotropy behaviour.

Table 2. Recovery ratio of components B during the thixotropy test.

Sample	G’ Baseline	G’ Regeneration	Recovery Ratio
B RELIABLE	1.01E+4	4.00E+3	0.40
B PROBLEM	6.03E+0	4.71E+0	0.78

Chemical analysis

The IR spectra of A RELIABLE and A PROBLEM didn’t reveal significant differences between the samples (see Fig. 7) as both spectra are almost superimposed.

The major component was DGEBA (Bisphenol A diglycidyl ether).

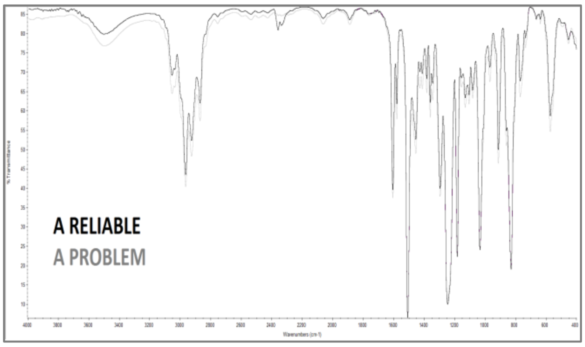

Figure 7. IR of components A

The bands appearing in the IR spectra of B RELIABLE and B PROBLEM show the presence of an amino ether of propylene oxide (a cross-over agent) as the major component. There are no significant differences in both samples (see Fig. 8)

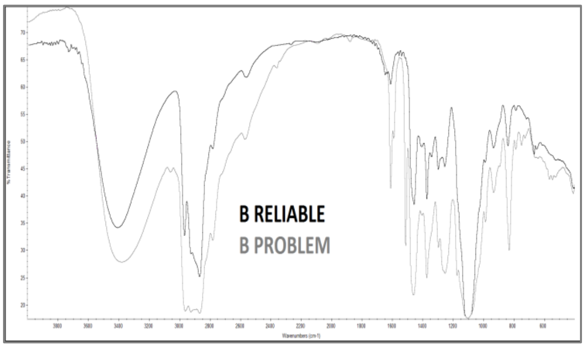

Figure 8. IR of component B

By analyzing the results for ash residue and solvent extracts on the four samples (see Table 3 and Table 4), we can see significant differences between samples named RELIABLE and PROBLEM in ash residues (connected to the inert filler content) and in solvent extracts (related to the amount of active raw materials).

Table 3. Acetone extract of components A

ANALYSIS	A RELIABLE	A PROBLEM
Ash (g/100g)	40.1	48.5
Extract (g/100g)	59.5	45.5
Ash plus extract (g/100g)	99.6	94.0

Table 4. Acetone extract of components B

ANALYSIS	B RELIABLE	B PROBLEM
Ash (g/100g)	51.5	52.5
Extract (g/100g)	39.8	15.5
Ash plus extract (g/100g)	91.3	68.0

CONCLUSIONS

The samples named PROBLEM were clearly adulterated by increasing the inert filler content or by reducing active raw material or by dilution, as can be seen from the chemical analysis. Rheological analysis shows significant differences in yield point, thixotropy and time behaviour. Both techniques can explain the unsatisfactory performance of the epoxy adhesive and the evident fraud. Nevertheless rheological analysis gives us more useful information, a quicker time-response and with a significant less amount of sample, all issues that could be very important in controversial instances.

REFERENCES

1. Yao, M.L. and Patel, J.C. (2001), “Rheological Characterization of Body Lotions”, *J. Applied Rheology*, **11**, 83-88.

2. ASTM D3677 – 10e1 Standard Test Method for Rubber Identification by Infrared Spectrophotometry.

3. ASTM D297 – 93(2006) Standard Test Methods for Rubber Products-Chemical Analysis.

4. Mezger, T.G. (2006), “The Rheology Handbook”, Vincentz, Hannover, pp. 128-131.

5. Mezger, T.G. (2006), “The Rheology Handbook”, Vincentz, Hannover, pp. 144-150.