

IMPORTANCE OF THERMOANALYTICAL METHODS FOR QUALITY CONTROL IN THE  
CAR BUILDING INDUSTRY

H. Nömayr and H. Rothbächer

Dept. Quality Control, BMW, P.O.Box 1120, D-8312 Dingolfing, F.R.G.

ABSTRACT

Mechanical and dynamic methods of thermal analysis are most advantageous for quality control of inorganic and organic materials which are used in car building industry.

INTRODUCTION

In the last years, customers as well as ecologists demanded an increasingly higher standard as far as cars are concerned.

In order to fulfill these demands, the tolerances of the physical and chemical properties of the material were more and more limited.

New, high-grade-materials like micro-alloyed sheet-steel, fibertightened plastics etc. and increasingly complex production-techniques as for example cathaphoresis, gasnitridation and so on were used.

By using conventional methods of research, the intense accuracy of testing organic materials, which is of great importance, was not to be achieved or only ineconomically.

Thus, there was the need to look for better and improved testing methods.

So we decided to use Thermal Analysis. In our opinion, the main advantage is to be found in the mechanical and dynamic methods of Thermal Analysis.

METHODS

Thermodynamic methods supply us with the possibility to discover the optimal hardening temperature of polymers for instance decor paints and electrophoresis coating.

In our case decreased and phosphated test sheets were coated with cathodic electrophoresis coating in the same conditions as in production. The coating was reacted at different degrees of

temperature at constant coating time.

From those sheets, we prepared some specimens of about 5 mm radius.

A probe is excited by a frequency and power generator. A square formed oscillation affects the coating, that is to be tested according a time-temperature dependence.

The degree of elasticity, penetration, glass-transition-point and distortion of the square oscillation informs us about the mechanical properties and then about the degree of reaction of the polymers.

#### RESULTS AND DISCUSSIONS

After electrochemical coating of the car-bodies pre-treated, the coating is still gluey and (quite) soluble.

In order to give the coating the necessary stability against mechanical and chemical load, the polymer must be reacted by temperature. The degree of reacting mainly depends on the formula and the reacting conditions.

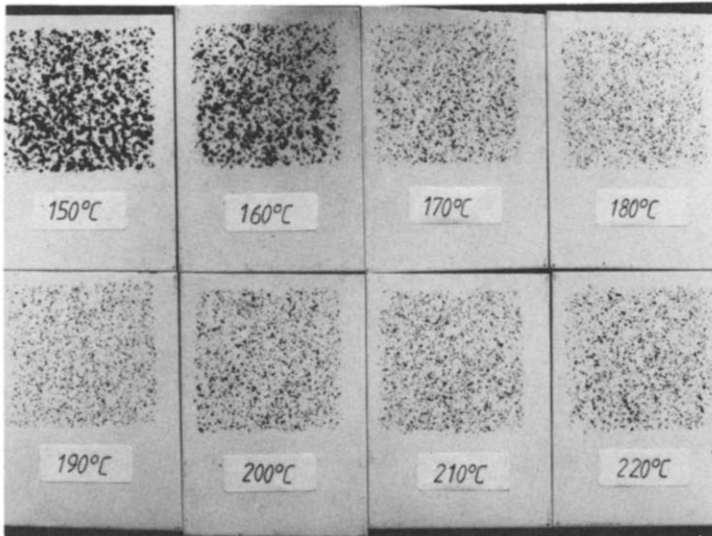


Fig.1 The picture shows test sheets, coated with cathodic electro coat (KEC).

The coating was treated as mentioned before with sheet-temperatures between 160°C and 220°C during a period of 17 minutes.

The further layers of lacquer coating were applied under ideal conditions in the laboratory, 14 min at 155°C and the top coat 14 min at 145°C. The lacquered sheets were exposed to the mechanical strain of sone-chip-test (DIN 53154).

As to be seen in the picture, the test shows, that the destruction of the laquer coating down to the steelsurface decreases as far as about 190°C under increasing reaction temperature and then the degree of potential corrosion is also deminished.

No improvement could be achieved in that respect when more than 190°C were applied. This test showed a different effect when sheets were treated at a temperature between 190°C and 220°C.

The higher the reaction temperature is, the more problems grow as to intercoat-adhesion between filler and KEC. We need not mention why both effects are unbearable for high-quality coating lavers.

The following diagrams show the change of the mechnic-dynamic property of KEC-layers as they are dependent on the degree of reaction.

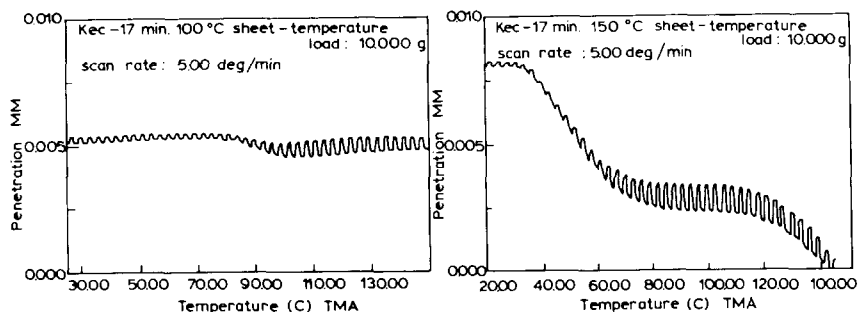


Fig. 2/3

In the series of diagrams a shifting of the glass-transition-point is to be realized at an increasing reaction temperature. It is also to be seen that increasing reaction temperature causes a shift of the glass-transition-point ( $T_G$ ).

In the same way a considerable decrease of the penetration can be shown.

In many cases lower object-temperatures than desired can be realized in body zones of high mass or in zones that are disadvantageous for streamlining. The range of the object-temperatures in a car body is the bigger the shorter the heating time of the body is. To compensate this temperature-dificit you can use increased air-circulation temperature. The air-circulation temperature, however, can only be increased within small limits as, otherwise, increased reaction or oxidation-effects on laquer material are likely to appear. The consequence would be that well-known intercoate-adhesion problem when KEC is cured within a longer period KEC than is proper.

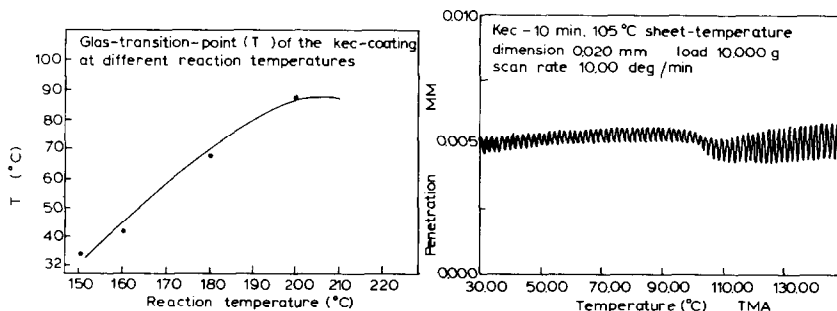


Fig. 4/5

At a constant curing temperature and variation of curing time the change of the reaction-degree is less significant, as shown in the picture.

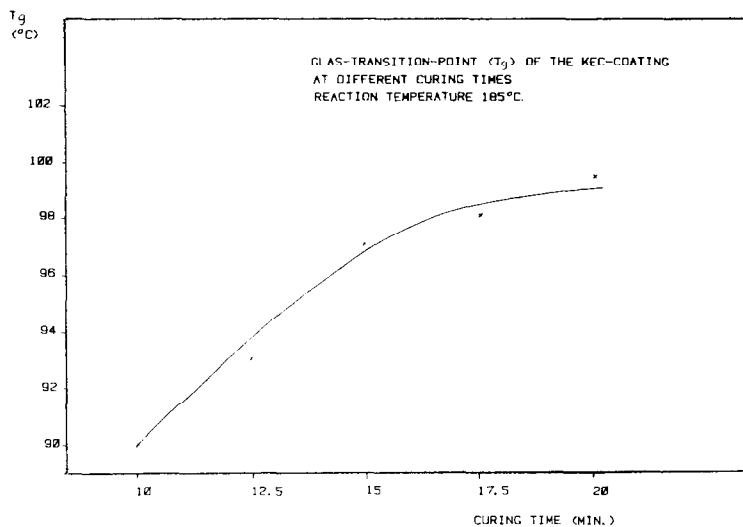


Fig. 6

$T_G$  when it is shown in dependence on curing temperature offers exact hints towards the degree of reaction.

This method is practised at BMW in order to compare of high-developed coating-materials (for ex.KEC, filler, to coat). In this way information can be achieved about the reaction behaviour of the coating.

An improvement of the method can be obtained when the E-modulus of the varnish-coating is described in dependence of time and temperature.

Today the operation demands too much time, because the deformation-oscillations, in this case saw teeth curves, must be evaluated graphically each saw-tooth for its own.

In the near future we hope to get a suitable software to evaluate the results automatically by computer-assistance.

Another application of thermal analysis is dealing with investigations of lubricants. The method of differential-calorimetry is preferred.

In metal-cutting the result strongly depends on the nature and the quality of the material, of the tool, of the precision of the machine and the choice of the suitable lubricant.

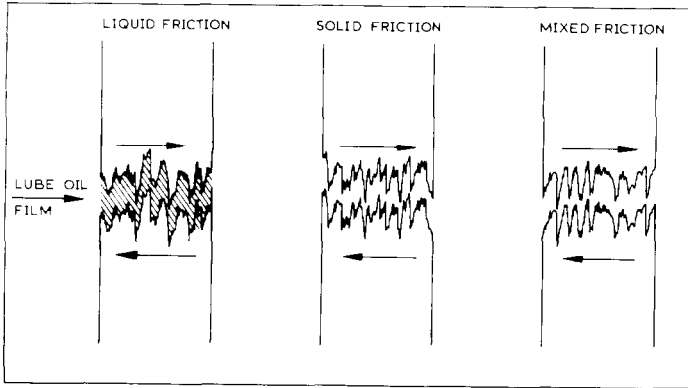


Fig. 7

The cutting takes place under conditions of "mixed friction". Thus, there is a lack of oil-lubrication. In order to avoid local welding of the tool and the workpiece lubricants are used in addition to other substances, including materials extreme-pressure-additives. These additives are based on phosphorus, sulfure and chlorine.

If local overheating occurs in consequence of high friction moments, ghis additives react to form Fe-phosphates, -sulfides or -chlorides, which prevent a direct contact from metal to metal and thus welding.

If these EP-additives respond too quickly, that means at lower temperature, Fe-phosphates,-sulfides or -chlorides are generated on the tool which should be avoided. This causes an increasing wear of the tool. The tool-life-time and by that the machine-availability are reduced. If the EP-additives respond too late, that means at too high temperatures, welding between tool and workpiece or the span occurs.

Pickups on the cutting edge affect the dimension-stability and the quality of the surface.

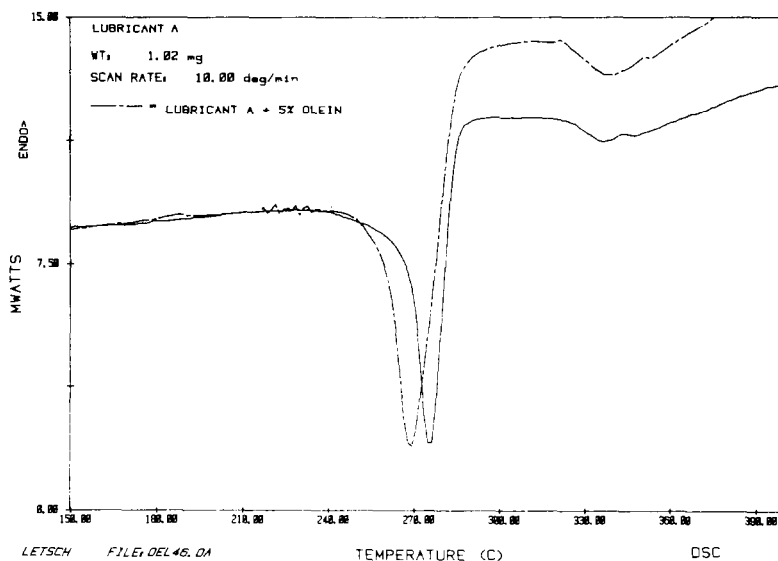


Fig. 8

In this case help of a new lubricant with EP-additives basing on Zink-Dialkyl-Dithiophosphate and anti-wear-additives basing on fatty-oils and Oleicacid tool-life-time increases about 20 %.

We tried to increase the tool-life-time by further addition of anti-wear additive and Oleic-acid. Instead the tool-life-time decreased 25 %. This effect was not to be explained at first. DSC investigations showed, that the activation-temperature of the EP-additives decreased about 7°C.

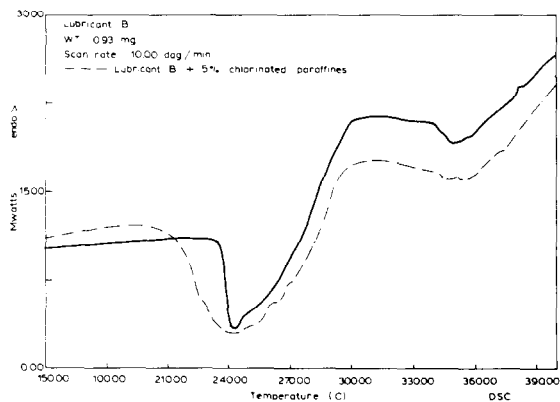


Fig. 9

In another case we obtained an improvement of about 25 % of the tool life-time, with the application of a different new lubricant.

By adding chlorinated paraffines we tried to improve the tool live-time beyond the obtained degree. However it decreased at about 15-20%. A considerable shift of the exothermal reaction curve was obtained just as it was seen in the preceding example.

In our view, this process can be explained by the fact that oleic acid is added and thus Zn-DDP is destabilized. We see a similar process in the second case. Thermal stress causes that chlorinated paraffines separate acidic compounds that catalyse the decomposition of Zn-DDP. The destabilisation of the EP-additives causes a shift of the activation-temperature of Zn-DDP to lower temperature ranges and thus higher wear is the consequence.

By means of this procedure a preliminary choice of lubricants can be made. That selection can only be made, when production parameters are really well known.

#### CONCLUSIONS

In material testing thermoanalytical methods have proved successfull. The experiences show, that a close cooperation between user and producer of the system is necessary. Institutes, users and system producers are requested to publish their experiences in order to intensify the applicability of the technique.

As to the near future a standardisation of the thermoanalytical methods is necessary. As suggestion the recently created standardisation of elastomer-investigation by IR-techniques could be helpful.