Adhesives Rheology

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Introduction

Understanding the formulation and performance of adhesive systems requires a combination of many disciplines. Rheology is one of these. The question to give an answer is:

-what is the benefit of rheology for adhesive testing
-how should rheology be applied effectively to maximize this benefit.

All adhesives must flow into the substrate surface to establish a good bond. Thus viscosity is an essential parameter. Furthermore adhesives are subjected to high deformation rates during coating or extrusion processes. Thus the viscosity as a function of rate or time i.e. frequency also becomes important. Adhesives have to perform over a wide temperature range, which requires additionally a good knowledge of the temperature dependence of the viscosity. Consequently, viscoelastic testing is one of the approaches for adhesive characterization.

Dynamic mechanical analysis (DMA) is a rheological technique which provides this information. Dynamic mechanical measurements are being increasingly used because of some inherent advantages: short testing times, very good reproducibility and small samples - thus DMA is ideal for screening tests in order to establish the desired relationship between adhesive formulation and performance.

DMA and viscoelastic measurements

The standard DMA technique involves the probing of an adhesive sample under oscillatory shear between parallel plates (Fig.1). The frequency of the oscillation relates to the shear rate/time dependence of the adhesive sample. Such a test provides the following viscoelastic parameters:

-\(G'\), the storage modulus represents the elastic deformation of a material and is a measure of the hardness of the adhesive at a given temperature. A typical hot melt has a \(G'\) at 25\(^\circ\)C, varying from \(10^7\) to \(10^8\) Pa. A good PSA has a value of \(10^4\) to \(10^5\) at room temperature.
-\(G''\), the loss modulus is associated with energy absorption mechanisms and correlates to the viscous deformations in a material i.e. it represents in a sense the flexibility of an adhesive.
-\(\eta^*\) is the complex viscosity and correlates in the fluid state to the flow resistance of the adhesive.
-\(\tan \delta\) is the balance between the viscous and elastic behaviour of an adhesive. In practice, \(\tan \delta\) correlates well to the cohesive strength of an adhesive for \(\tan \delta < 1\).

Fig 1: DMA technique
Hot melt adhesives

Hot melt adhesives, as the name implies, are thermoplastic systems which are applied in the molten state. They flow into both substrates and then rapidly cool to a tough adherent solid. Relative comparisons of the performance parameters such as open time, hot tack, setting time and cold crack can be obtained from a simple viscoelastic characterization. Usually wax diluents and resin tackifiers are added for optimum performance. Fig 2 and 3 display the viscoelastic properties $G'$, $G''$ and tan delta as a function of temperature for two book binding hot melts with different application properties (general purpose and pronounced lay flat properties). The two figures are quite different. Note, that not only the absolute values of $G'$ and $G''$ are different, but also the area between the two curves. Tan delta describes the relative behaviour between $G'$, the elastic, and $G''$, the viscous contributions, which is a measurement of the cohesive strength of the hot melt. The storage modulus $G'$ defines the hardness of the hot melt at the use temperature. Lower tan delta values indicate better cohesion but less flexibility. A window for general purpose hot melts at room temperature has been identified in $G'$ as $5 \times 10^7$ to $10^8$ Pa and tan delta as 0.1 to 0.3.

At low temperatures, both adhesives have similar hardness as can be seen by the $G'$ values. The loss modulus $G''$ shows a maximum at low temperature, around $-10^\circ$C for sample A and at $0^\circ$C for sample B. The peak temperature of $G''$ for the low temperature transition correlates with cold crack predictions, which defines low temperature flexibility (cold crack is the temperature at which a hot melt will fail under bending deformation). Cold crack can also be related to the $G''$ maximum temperature with the value of tan d at that temperature also having some effects. The higher tan delta at the given temperature, the greater the energy dissipation, the lower the cold crack temperature. Sample A has a cold crack temperature of between $-15$ to $-10^\circ$C and sample B between $-5$ to $0^\circ$C, which correlates very well with the predictions of the viscoelastic material response. Over the whole working range (0 to $50^\circ$C), tan d for sample A is much lower than for sample B, indicating a higher potential for cohesive strength. However sample B is more flexible due to the high tan delta and as such more suitable for lay-flat properties. At $60^\circ$C, tan delta for sample A increases rapidly due to
the melting of the crystalline structure of the wax. The lack of a clear melting point in sample B is an indication of a much lower wax content.

The setting time of a hot melt is related to its cooling curve. The viscosity should remain low enough for the substrates to be brought in contact and then rise rapidly to set the bond in a minimum of time. The setting time for a book binding compound can be seen as the time required for an adhesive to obtain sufficient hardness in order to continue eg. with trimming. This time can of course be reduced by decreasing the application temperature (which may have other negative effects) or by modifying the viscoelastic behaviour of the hot melt. Assuming a critical value of G' of 10^7 Pa gives sufficient strength to the bond in a typical book binding application, the sample A in Fig. 4 shows a setting temperature of 47°C and for sample B of 22°C. Clearly, the setting time for sample B is longer than for sample A under identical operation conditions.

Open time is another performance parameter, which can be easily determined on a relative basis of the viscoelastic measurement. A hot melt is open when it is capable of flowing and wetting-out a substrate. Upon cooling, i.e., once a certain hardness has been reached, together with a cohesive strength, the hot melt is no more longer open. This critical point for hot melts can be correlated to tan delta = 1. For adhesive A, the critical value is obtained at 65°C, for adhesive B at 54°C. It follows that sample B has a longer open time under identical processing conditions.

Structural adhesives / 2 /

Structural adhesives are usually thermosetting polymers. They are applied to the substrate as a low viscous, reactive liquid. The viscosity increases rapidly as the adhesive polymerizes and crosslinks in the joint to form a rigid high strength bond. Epoxys and cyanoacrylates are important types of structural adhesives.

Viscosity, as a function of time and temperature is the important parameter for predicting pot life or clamp time. Fig.5 shows the viscosity eta* vs. reaction time for a typical epoxy structural adhesive. Curves like these can predict residence time (pot life) at a given temperature and curing times (clamp time, cycling times) in process equipments.
Fig. 6: Cure of a two catalyst system

Cure profiles are used by the chemist for formulating a resin to meet the needs of the application. Fig. 6 shows the cure of a two-catalyst system. The purpose of the second catalyst was to accelerate the initial part of the cure in order to provide a more rapid viscosity growth at the beginning (for easier handling) without altering the gel point and the final bond strength.

At the gel point the crosslinking resin changes from a liquid to a solid. At this point the viscosity goes to infinite. The gel point is important, because processing (shearing) above this point causes the forming network to break, which has negative effects on the strength of the bond. A good approximation of the gel point can be obtained by correlating this to tan delta = 1. At this point the moduli G' and G'' have a cross point. In a typical cure curve of an epoxy resin, tan delta goes through a maximum before reaching the gel point (Fig 7). Results from Winter et al. show that a more accurate prediction of the gel point is when G' becomes independent of frequency at low frequency/4/. This is, however, more of an academic consideration. Beyond the gel point, the modulus builds up to give the adhesive its ultimate strength.

Fig. 8 shows the storage modulus G' and tan delta for a cured epoxy adhesive system. While the modulus below the glass transition correlates with the adhesive strength, the glass transition temperature itself is an indication of the extent of the cure and also defines the upper use temperature.

Pressure sensitive adhesives

Pressure sensitive adhesives (PSA) are highly viscoelastic and their performance correlates directly to the viscoelastic behaviour of the bulk adhesive as well as to the surface properties of the adhesive and the substrate itself. Making a bond involves a deformation at low rate. The adhesive flows
into the substrate and forms a bond when the flow and surface properties are favourable. Fig. 9 shows the changes in the storage modulus $G'$ as a function of frequency or rate. Application rates for tapes can be found around 1 1/s. Bond strength, the major performance parameter is tested by performing a peel or a tack test. The peel test is a debonding test at high rates, the tack test is performed at a low rate. The cohesive strength of a PSA can be measured using a shear test, which is a creep test for most of the time. This test is a very low rate, low frequency process. All bonding and debonding processes, as shown in Fig. 9, can be related to the viscoelastic behaviour of an adhesive. Investigations by Chu / 5 / show, that a PSA must have a storage value of between $5 \times 10^4$ Pa and $1 \times 10^5$ for a high cohesive strength tape at use and application temperature. A typical adhesive DMA plot is shown in Fig. 10. / 6 /. The $G'$ value at room temperature is $5 \times 10^4$ Pa. For most elastomers however, the modulus $G'$ at room temperature is higher. In order to bring the values of $G'$ into the application window, a compatible tackifying resin and/or oil needs to be added. Another determining factor for a well performing PSA is the glass transition of the rubber. Highly cohesive strength adhesives at room temperature give optimum performance for a tan delta peak between -10 and +10°C. The addition of a compatible resin reduces the storage modulus at room temperature and also gives a rubber glass transition at higher temperatures. The addition of oil only reduces the modulus, because of its very low transition temperature. Using this procedure, any suitable elastomer can be driven into the PSA application window as shown in Fig. 11.

This now provides only one value for the viscoelastic properties, which correlates to the performance at room temperature. The viscoelastic properties need to be known for a larger temperature range in order to predict total adhesive performance (e.g. chill or deep freeze labels (-20 to 40°C)). A good adhesion at -20°C demands for a correct modulus at this temperature and an appropriate loss tangent peak temperature. An adhesive performing over a wide temperature range needs a low tangent peak and the correct plateau modulus over as wide a temperature range as possible. If the storage modulus values, $G'$, are greater than $10^8$ Pa, as approaching the glass transition, the bond becomes very weak. Shear resistance at room
temperature and higher temperatures is another important performance criterion. Shear or creep is a low rate process. According to the time/temperature superposition principle, the high temperature region corresponds in effect to the low frequency (rate) region of a frequency test run at a constant temperature. It follows that the higher the temperature of the $G'$ and $G''$ cross over point, as shown in Fig.12, the greater the shear resistance. The cross over point temperature and its absolute value are good parameters to correlate with the shear resistance

![Fig.12: PSA and shear resistance](image)

an ideal technique for screening experiments in product development.

Rheology is also an excellent quality/process control tool. Due to the advantages, mentioned above, rheological measurements are the choice, especially with the prices of good rheological instruments coming down.

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References

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Conclusions

Dynamic mechanical measurements can help formulate and predict adhesive performance of hot melts, structural adhesives and pressure sensitive adhesives. The benefit of such an analysis is that the measurement of the viscoelastic properties is quick (a couple of hours) and the correlation of the viscoelastic parameters is easy to establish, whereas traditional performance evaluations may take weeks.

Rheology is a vehicle to relate product formulation to performance. The benefit is speed and sensitivity, and as such rheology is