AN001

Hot Melt Adhesives

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BACKGROUND

Hot melt adhesives are thermoplastic polymer systems applied in a molten state. They must flow smoothly onto both surfaces and then rapidly cool to a tough, adherent solid at room temperature. Thus, viscosity as a function of temperature is a key to proper hot melt performance.

STICKY VS. BRITTLE

Many hot melt adhesives are supplied as pellets. A pelletizing operation for a new material can be troublesome if the material is too sticky or too brittle. Measurement of the elastic (storage) modulus *G*' as a function of temperature can guide the adhesive chemist in adjusting the adhesive formulation to optimize the pelletizing operation. Figure 1 shows data obtained from dynamic mechanical measurements for a polyamide copolymers. The maximum in each tan δ curve corresponds to the glass transition temperature of the sample. The elastic properties (G') above the glass transition temperature are especially interesting. Sample A was too brittle and tended to shatter into glassy fragments during pelletization. In contrast, Sample C was sticky and gummed up the pelletizer. Sample B was optimum, resulting in the proper values of the glass transition temperature and elastic modulus with good pelletization and adhesive properties.

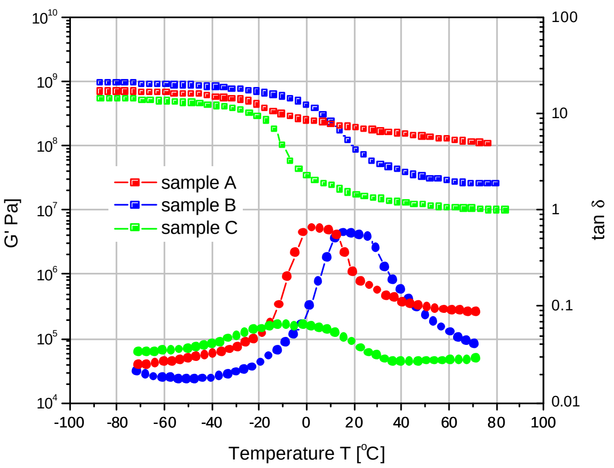

Figure 1: Glasstransition of 3 Polyamide Copolymers determined at 10 rad/s

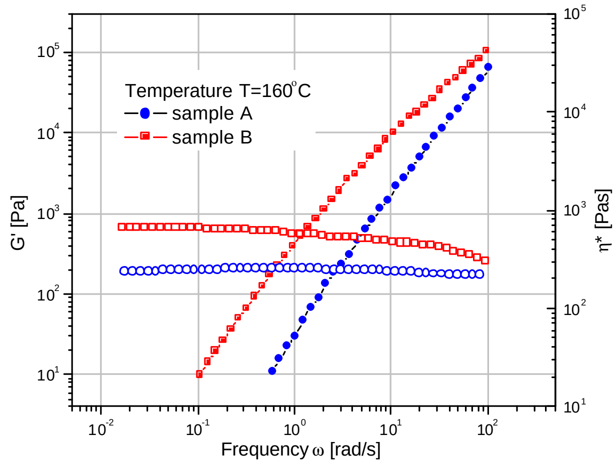

Figure 2: Effect of MWD on the viscosity and elasticity of a polyamide hot melt

HOT MELT VISCOSITY

In processing, the viscosity must be fairly low at application temperature to allow good substrate penetration. If it is too low, it runs off the substrate or produces a thin film which results in voids when two substrates are joined. The hot melt viscosity should remain low enough for the opposite substrate to be brought into contact and then rise rapidly to set the bond in a minimum time. The molten viscosity of most adhesive polymers (low molecular weight) is proportional to its molecular weight.

EFFECT OF MOLECULAR WEIGHT ON VISCOSITY

Rheology provides the key to the relationships between viscoelasticity, molecular structure and processing performance. The molecular structure of the polymer system, and the rheology determine the behavior during processing. Perhaps the best known relationship between molecular structure and processing is the effect of molecular weight on viscosity. The limiting low frequency viscosity is strongly dependent on molecular weight. Two adhesives differing in molecular weight are shown in Figure 2. Molecular weight, molecular weight distribution, branching, and crosslinking affect the viscosity and the elasticity of melts and as such also the polymer processing and mechanical properties.

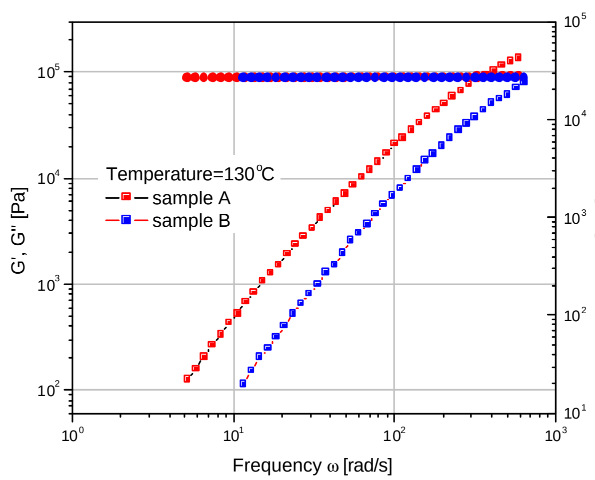

Figure 3: Polyamide hot melt samples with the same viscosity, but different eleasticity

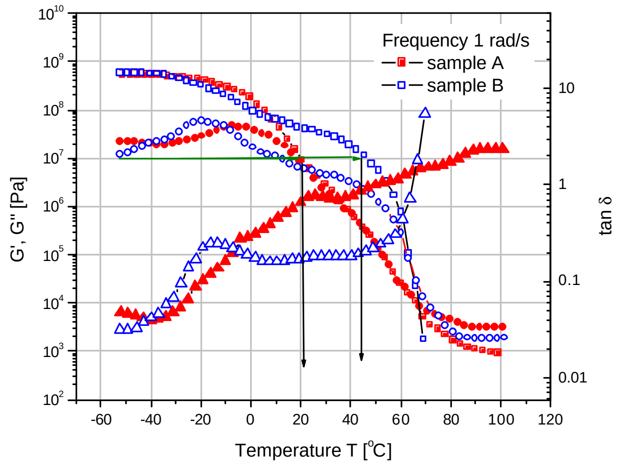

Figure 4; Hot melt adhesive with different peromance regarding flexibility and toughness

Generally, hot melt adhesives are Newtonian; that is, their viscosity is independent of frequency, as shown in Figure 3 for a polyamide adhesive. These data show identical viscosities for two samples of a polyamide adhesive that processed differently. The higher elasticity of Sample A was traced to more branching during polymerization.

TOUGHNESS VS. FLEXIBILITY

Another important requirement of a hot melt adhesive is toughness and flexibility in the solid state. It must not become brittle at the expected use temperature. Dynamic mechanical measurements provide the best approach to establish these adhesive properties. Figure 4 shows the dynamic mechanical behavior as a function of temperature for two book binding hot melts with different application properties (general purpose and pronounced lay flat properties). The differences in storage modulus (elasticity) indicate a significant performance difference at use temperatures. The level of *G'* at application temperature (at room temperature) describes the hardness and flexibility of the adhesive. Tan δ , the ration between viscous and elastic contributions of the modulus is a measure of the cohesive strength of a hot melt. Lower tan δ indicates better cohesion. but less flexibility. A value of tan δ from 0.1 to 0.3 at room tempertaure is an optimum for a general purpose hot melt. The loss modulus G" shows a maximum at low

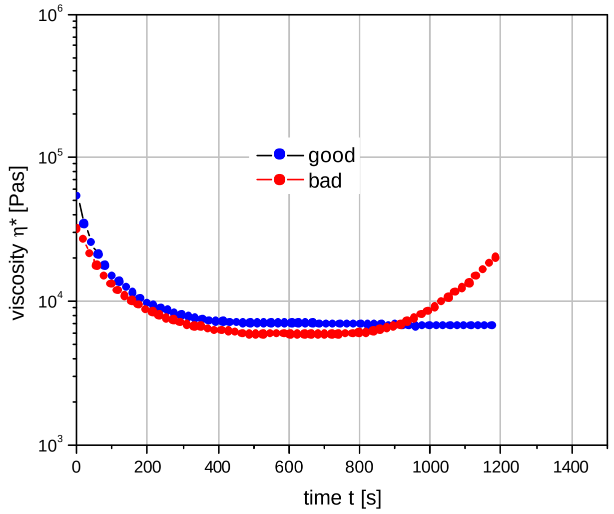

Figure 5: Pot Life of two hot melt adhesives

temperature for both samples, i.e. -10 °C for sample A and 0°C for sample B The transition peaks relate to increased toughness and correlate with cold crack predictions. Cold crack is the temperature at which a hot melt will fail under a bending deformation. The cold crack temperature for sample A is between =-15 and -10 °C, for sample B between -5 and 0 °C., which correlates well with the predictions of the viscoelastic response. Over the temperature range from 0 to 50 °C, the tan δ of A is significamtly lower, than for sample B indicating a higher cohesive strengt. Sample A however is more flexible (higher Modulus) and as such more suitable for lay-flat properties. At 60 °C. tan δ for sample A increases rapidely due to melting of the remaining crystaline structure. The lack of a clear melting point in sample B is a proof of much lower wax and lower crystaline content.

SETTING TIME, OPEN TIME, POTLIFE

The setting and open time of a hot melt are related to the cooling curve. The setting time is defined by the time, the viscosity remains low enough for the substates to be brought in contact before rising to set the bond. The setting time for a boook binding compound can be seen as the time for the hot melt to obtain sufficient hardness before performing the next process step. A critical hardness, G' approximately 10^7 Pa, gives sufficient strength to the bond in a typical book binding application and is obtained for sample A at 49°C and sample B at 22°C. (Figure 4) Sample B has a longer setting time then sample A under identical operation conditions.

The open time is another performance parameter, which can be easily determined from the viscoelastic measurement. The hot melt is open, as long as ot is capable to flow and wett-out the substrate. Upon cooling, once a certain hardness has been reached, together with the cohesive strength, the hot melt is no longer open. This critical point for a hot melt correlates well with the crosssover of G' and G" i.e. tan δ=1. For sample A this value is obtained at 65 °C, for sample B at 54 °C. Thus sample B has a longer open time under the same processing conditions.

The viscosity of hot melt adhesives must be stable at processing temperatures. Resins are frequently held for several hours in open tanks in dispersing equipment The time during which the viscosity does not change significantly is referred to as pot life. Figure 5 shows the viscosity versus time for a polyamide resin. The viscosity drops initially because of molecular weight reduction due to the absorption of water and then rises slowly for sample A. This is attributed to slow oxidative crosslinking. A new formulation (sample B) was developed that was stable for more than two hours at process temperatures, allowing for possible breakdown and changes in customer packaging lines.

CONCLUSION

Hot melt adhesives must have a good flow during application and be able to cool rapidely to form a tough adhesion. Factors that determine good adhesives are those which influence the rheology of adhesives, including molecular weight and other chemical structural features of the material. Rheological measurements can result in the development of improved hot melt adhesives and in the prediction of their performance

REFERENCES

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