RHEOLOGICAL ANALYSIS FOR DEVELOPMENT AND QUALITY ASSURANCE OF PRESSURE SENSITIVE ADHESIVES

Roland H. Horst, Ph.D., Analytical Scientist, Berry Plastics, Franklin, KY

Summary

Specifications of pressure sensitive adhesives list as the most important parameters peel and shear adhesion, and tack. Given a good thermodynamic interaction between an adhesive and its substrate, these three parameters are governed by the mechanical or flow properties of the PSA, its modulus or viscosity (hardness or resistance to deformation/flow) and their time and temperature dependence. For example, shear adhesion measures the time that a PSA tape can support a certain load. The PSA must be soft enough to conform to its substrate's surface, or even fluid enough to wet out, to enable bond formation. During the shear test, certain hardness is necessary to provide the PSA with enough cohesive strength to sustain the stress caused by the load applied to the tape. In designing adhesives, rheological testing, also called dynamic mechanical analysis (DMA), can help finding the best formulations and process conditions. The main focus will be on SIS based adhesives and how DMA can help in the development process. Correlations of characteristic parameters of the flow curves and of the tape specifications will be presented. The use of DMA for testing tackifier/polymer compatibility, giving directions for optimizing the formulation for a certain application, and determining the temperature application window will be demonstrated.

Morphology of Block Copolymers

Block copolymers as used in adhesives are mainly diblock or triblock copolymers of styrene as endblocks and isoprene (SIS) or butadiene (SBS) as midblock, see Figure 1. Star block copolymers are also used, the isoprene blocks are bonded together in the center of the star and the styrene endblocks are on the outside, giving them similar properties as the triblock copolymers. Block copolymers preserve the properties of the homopolymers in contrast to statistical copolymers, but the block copolymer geometry gives them mechanical properties very different from the homopolymers. Incompatibility between the endblocks and the midblock leads to phase segregation.

The morphology of block copolymer based adhesives resembles that of emulsions. There are small droplets of styrene phase in a continuous isoprene/butadiene matrix phase. Figure 1 shows a sketch of the morphology. There are many similarities between emulsions and the SIS adhesives. The polystyrene phase in an adhesive forms small spherical domains, like oil droplets in an oil-in-water emulsion. The oil droplets in the emulsion must be stabilized, otherwise they coalesce. This is achieved by adding surfactants. Block copolymers do not need stabilization of the morphology. A diblock copolymer has two different ends within one molecule, the styrene block and the rubber block in the case of SI, giving it capabilities similar to an amphiphile. Figure 1 shows the configurations for a diblock. 1' is the common case, with the styrene endblock in the disperse phase and the isoprene or butadiene block in the matrix phase. The much more uncommon case, 2', would be the entire chain in the matrix phase. These are the only two configurations possible for a diblock – neglecting the possibility that the isoprene/butadiene block can be found in the disperse phase. In contrast to emulsions, the domain size in a block copolymer is not variable. For a given molecular weight of the blocks only one size of droplets is found. The size of the styrene domains is very small and in many tests the phase separation is not obvious, they behave like homogeneous materials. This kind of morphology is called microphase separation.

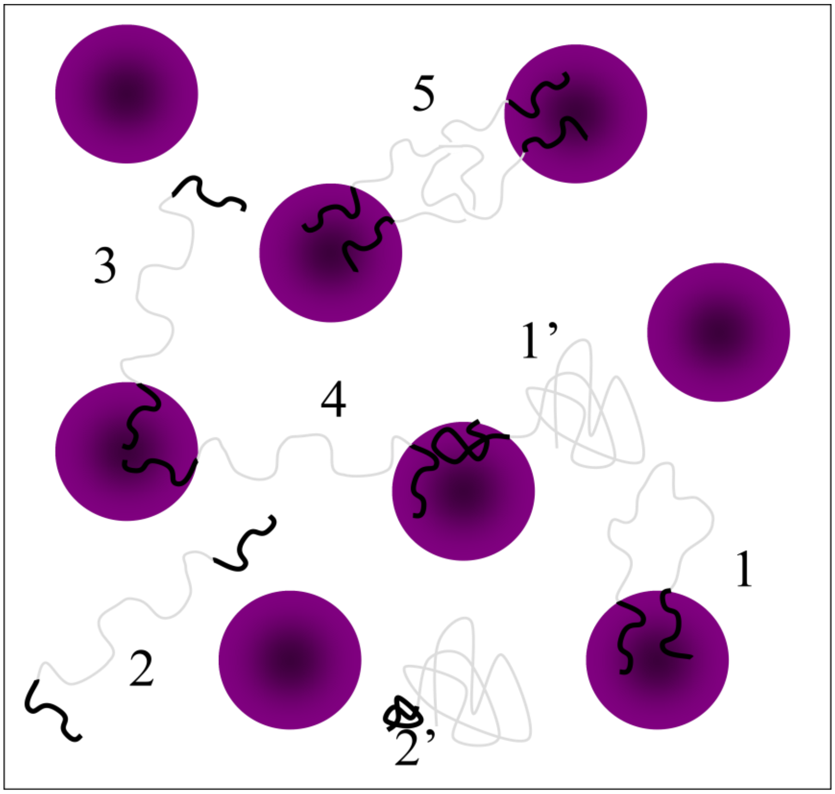

Figure 1. Sketch of the morphology of a block copolymer. The spherical polystyrene domains are shown dark, the continuous rubber phase is depicted white. The styrene endblocks are shown as black lines, the isoprene midblocks as thinner grey lines. 1’ and 2’ are the two possible configurations for a diblock copolymer, 1 through 5 stand for the triblock copolymer.

An oil-in-water emulsion has flow properties different from its base materials water and oil. If the amount of the disperse phase is high, it is very stiff and does not flow easily. The reason is that the droplets stay intact and resist flow. The moving particle is not a single water or oil molecule, but the entire droplet. If there are enough droplets, they limit their mobility and the viscosity of the macroscopic system increases dramatically as further oil is added. Block copolymers show this increase of the modulus as well. The effect is much more pronounced than for emulsion. The reason is the high glass transition temperature of polystyrene. At room temperature the styrene domains are glassy, hard spheres. Once formed, a block cannot be removed easily. The only way that movement is possible, is that the whole sphere moves, together with the large shell of surrounding isoprene blocks. Only at higher temperatures, above the glass transition temperature of the styrene domains is it possible to have free chains (2’ in Figure 1) that allow movement by a different mechanism. This is the reason that SIS and SBS block copolymers can be “melted”. The comparatively low molecular weights give them good processability and flow at elevated temperatures. When the temperature falls below the glass transition temperature of the styrene domain, the cohesive strength is restored. Their behavior is thermo-reversible.

Triblock copolymers exhibit properties not found in diblocks. They can be in similar configurations as the diblock, the free chain (2), a looped midblock with both endblocks in the same styrene sphere (1), or one free endblock (3). These three configurations will not give them different properties from those mentioned above. The two other configurations are the two end blocks in two different styrene domains (4) and interlaced loops (5). These two lead to fairly permanent ties between two styrene domains. The whole system will behave like a network with the styrene domains as the cross-links. This is very similar to gelatin gels in which the network is created by a triple helical structure that forms the cross-links for the network. The cross-links are not due to covalent bonds between different molecules but due to physical interactions, hence the name physical networks. Heating the gels removes the helices and the system liquefies. Cooling it again restores the triple helices and the gel forms. SIS behaves the same. At high temperatures, above the glass transition of the styrene domains, the droplets can release the end blocks, especially when stress is applied, and the system flows. Below the glass transition temperature, the endblocks are trapped in the styrene domains which then function as cross-links. Same as for gelatin, this is a thermo-reversible, physical network. SIS at room temperature behaves as a gel, a soft solid. Physical networks, same as chemical networks, can be broken when large stresses are applied. Physical networks, in contrast to chemical networks, due to the reversibility of the cross-links, can heal. This is demonstrated well by gelatin gels which can be liquefied by stirring. If left alone, they recover their elasticity. This works best at temperatures just below the thermal transition of gelation where the physical cross-links have better dynamics.

SIS adhesives contain, besides the block copolymers, other materials such as tackifiers, plasticizers, and other additives. Depending on their thermodynamic interaction, they will be found in the rubber phase (most common) and/or the styrene phase. This will change the volume ratio of the two phases and so change the domain size. The morphology found in SIS adhesives is most likely the spherical one shown in Figure 1. For higher ratios of endblock phase, other morphologies would be more stable, the cylindrical or lamellar morphologies for example. Flow properties of these materials are much more complicated since they are not isotropic. [1]

Rheology of Block Copolymers

Rheological testing measures how a material deforms when it is subjected to forces. For example, in the shear adhesion test, a weight is suspended from a tape. Gravity force pulls on the adhesive resulting in a very slow sliding motion of the tape. The corresponding rheological test is a creep test: A constant in-plane force is applied to an area of the tape (stress) and the tape will slide slowly downwards, the adhesive will show deformation (strain). Solids and liquids will behave very differently in this test. The deformation in solids follows Hooke’s law, the deformation is proportional to the applied strain. This is called elastic behavior. A typical example is a metal spring. The extension of the spring is proportional to the mass suspended from the spring. The extension does not depend on how long the weight force is applied or how fast. The proportionality constant between strain and stress is the modulus, G. Liquids, on the other hand, follow Newton’s law, the stress is proportional to the deformation rate. Liquids are viscous materials. When stirring a liquid in a bucket with a rod, the speed of the rod is proportional to the force applied. The speed (strain rate) does not depend on how long the liquid has been stirred or on the position of the rod in the bucket. The proportionality constant between strain rate and stress is the viscosity, η.

The typical test geometry for adhesive like materials is a parallel plate rheometer. The adhesive is sandwiched between two parallel disks, one of them is rotating, the other stationary. Knowing the geometry of the setup - plate diameter, plate distance, etc. - stress and strain can be calculated from the torque and the angle of rotation. Typically, adhesives are not tested in a steady shear test, i.e. a constant speed of rotation, but in oscillatory shear. The moving plate rotates back and forth with a given amplitude and frequency, resulting in sinusoidal stress and strain curves. The modulus determined in oscillatory testing, G*, and the modulus from steady shear testing, G, are related to each other [2]. The most common rheological test is a temperature sweep: The material is heated at a constant heating rate and continuously tested at a constant frequency. The shear amplitude is small so as not to change the material properties.

Adhesives are viscoelastic materials, meaning they combine properties of liquids (viscous) and solids (elastic). The modulus, G^*, can be separated in the viscous (G'') and the elastic component (G'). The combination of these two properties can be illustrated by a rubber ball dropping from a certain height. The ball will bounce on the floor and come up again, but not all the way. During the bounce some energy was transformed into heat, there is a loss of mechanical energy. This is described by the loss modulus G". When the ball touches the ground it deforms and then snaps back to its original shape making the ball jump up again. A part of the mechanical energy was stored during the bounce. This is quantified by the storage modulus G'. Another commonly used quantity is the loss tangent tan δ. The loss tangent is the ratio of loss and storage modulus. Values greater than unity characterize viscous materials, lower than 1.0 elastic materials. A material for sound dampening requires a high value for the loss tangent at the application temperature, so that the acoustical, i.e. mechanical energy can be absorbed.

Interrelation of Rheological Behavior and Adhesive Properties

Figure 2 shows a typical flow curve for a block copolymer based pressure sensitive adhesive. At very low temperatures the adhesive is hard and brittle, the modulus is very high and the loss tangent has very low values. When the glass transition temperature, T_g, is reached, it softens, i.e. the modulus drops sharply and the loss tangent reaches high values. T_g is defined as the location of the maximum of the loss tangent. Above T_g, within a wide temperature range, the modulus stays practically constant. At very high temperatures the styrene domains soften and the adhesive melts. Storage and loss modulus intersect at the cross-over temperature T_x. A more extensive discussion of how the adhesive properties relate to the rheological data can be found in references [3] and [4]. Here only a short description will be given. All rheological data in this paper are taken from temperature sweeps at an angular frequency of 1 rad/s and a heating rate of 3 °C/min. The rheometer used was a TA Instruments ARES RDA-3.

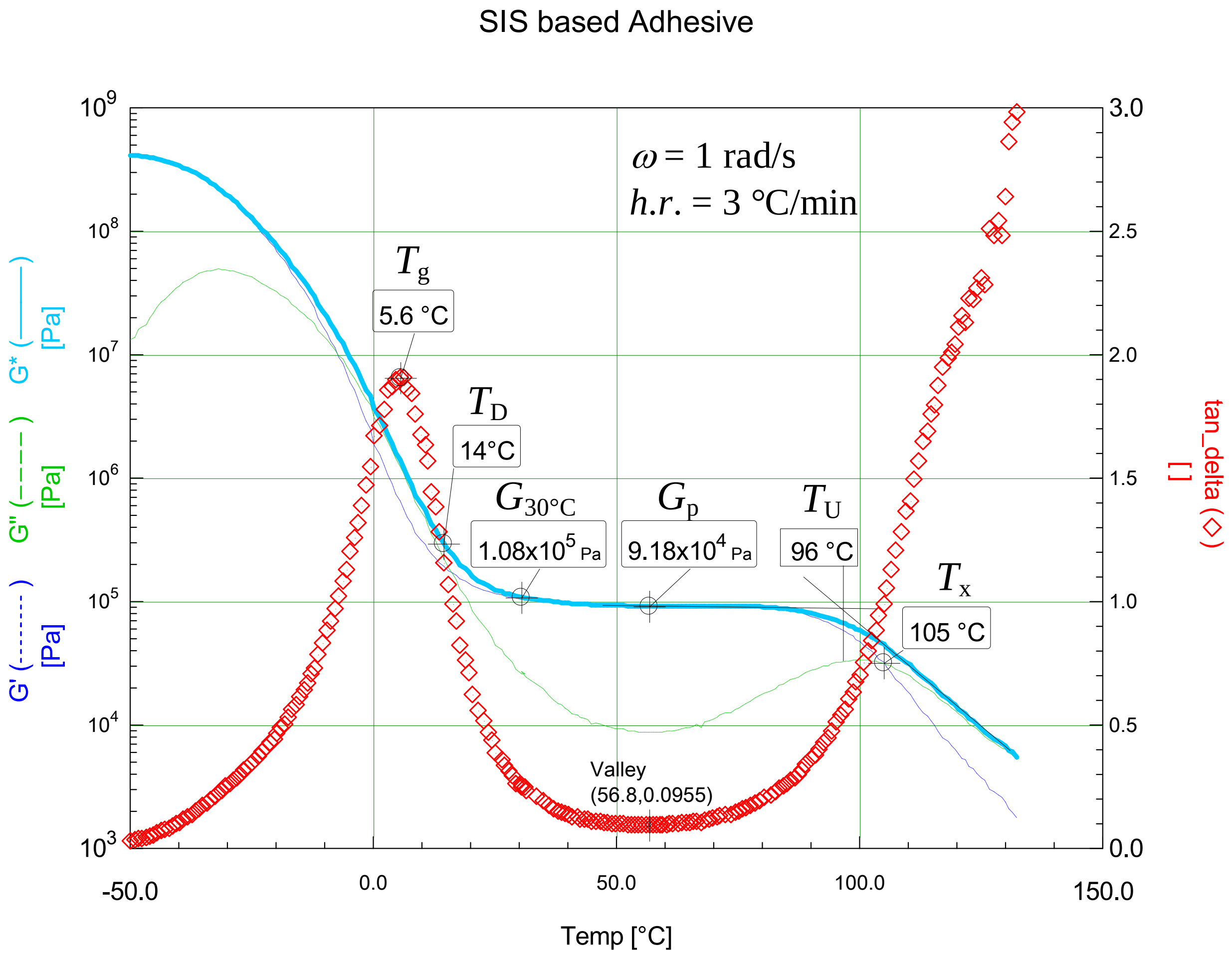

Figure 2. Temperature sweep of a block copolymer based pressure sensitive adhesive. G*: complex modulus, solid line; loss tangent tan delta, symbols.

Temperature Application Range. The Dahlquist criterion [5] states that the modulus should be between 50 and 300 kPa. If it is higher, the adhesive has difficulties wetting the substrate; if it is lower the adhesive has no shear resistance. The temperature where the modulus drops below 300 kPa is labeled as **Dahlquist temperature, T_D**, in Figure 2. For that adhesive it is about 10 °C higher than the glass transition temperature. The difference can be much larger, depending on the width of the glass transition and the plateau modulus. T_D is the lower temperature limit for application of an adhesive to a substrate. A good estimate for the upper end of the application range is the (extrapolated) end of the modulus plateau (96 °C in Figure 2).

Peel Adhesion. The peel adhesion test subjects the adhesive to a complicated deformation pattern and a flow that is not only shear flow. The shear rates reached in the test are higher than the one used for the temperature sweep. According to the time-temperature superposition principle, the rheological properties at lower temperatures than the test temperature have a major influence, i.e. a high modulus of the adhesive a temperatures below the test temperature (usually room temperature) is advantageous. Looking at the curve in Figure 2, this is the case when the **glass transition temperature, T_g,** of the continuous isoprene phase is not too far away from room temperature. Therefore, if the formulation is varied so that T_g moves to higher temperatures, the peel force will increase. This is shown in Figure 3.

Raising Tg even further would eventually lead to a decrease in peel adhesion due to decreased wetting abilities.

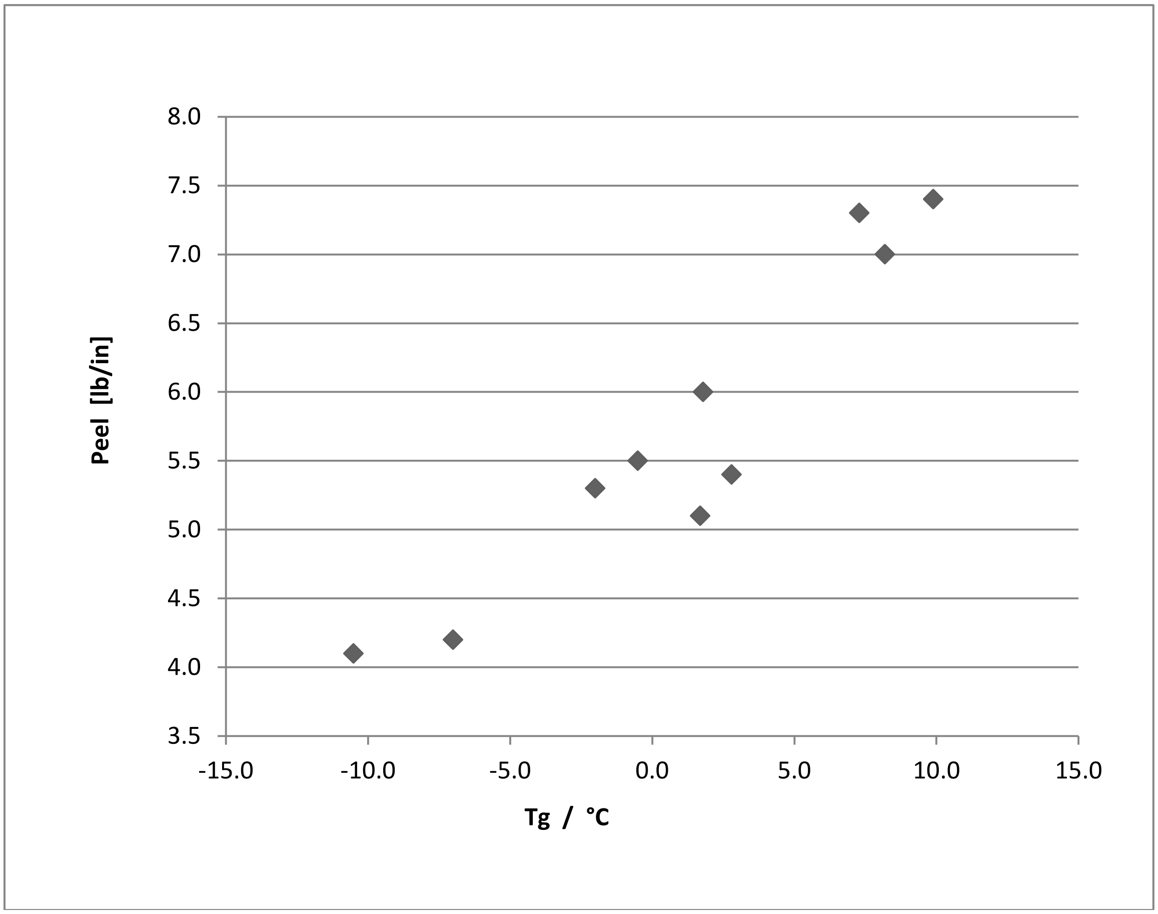

Figure 3. Dependence of peel force on the glass transition temperature for adhesive made of the same raw materials at different concentrations.

Tack: Tack measures the ability to form a bond to a substrate in a very short contact time. Good wetting is essential for good tack values. This means the modulus at the test temperature must be low enough to allow wetting but high enough to sustain a load. The block copolymer based adhesives show a broad temperature range where the modulus is almost constant. Often the modulus at 25 or 30 °C is used to characterize them. If the glass transition is very high its influence might still be felt at these temperatures and a better parameter might be the modulus at the temperature where the loss tangent has a minimum. This is indicated as **plateau modulus, G_p**, in Figure 2. No direct relation between G_p and tack could be found for the set of adhesive formulations. There are other parameters that have a great influence on the tack, for example the elasticity of the adhesive, the value of the loss tangent. Moving the softening point to lower temperatures also increases tack.

Shear Adhesion Failure Temperature, SAFT. At higher temperatures the glass transition of the styrene domains is reached and they soften. They do not longer act as stable physical cross-links; the network is dissolved and the elasticity decreases, as can be seen in the rapid increase of the loss tangent at high temperatures. At a certain temperature where the loss tangent is 1, the curves for storage and loss modulus intersect. This temperature is labeled as **cross-over temperature, T_x**, in Figure 2. There is a very good relation between T_x and SAFT as shown in Figure 4. SAFT is about T_x + 15 °C.

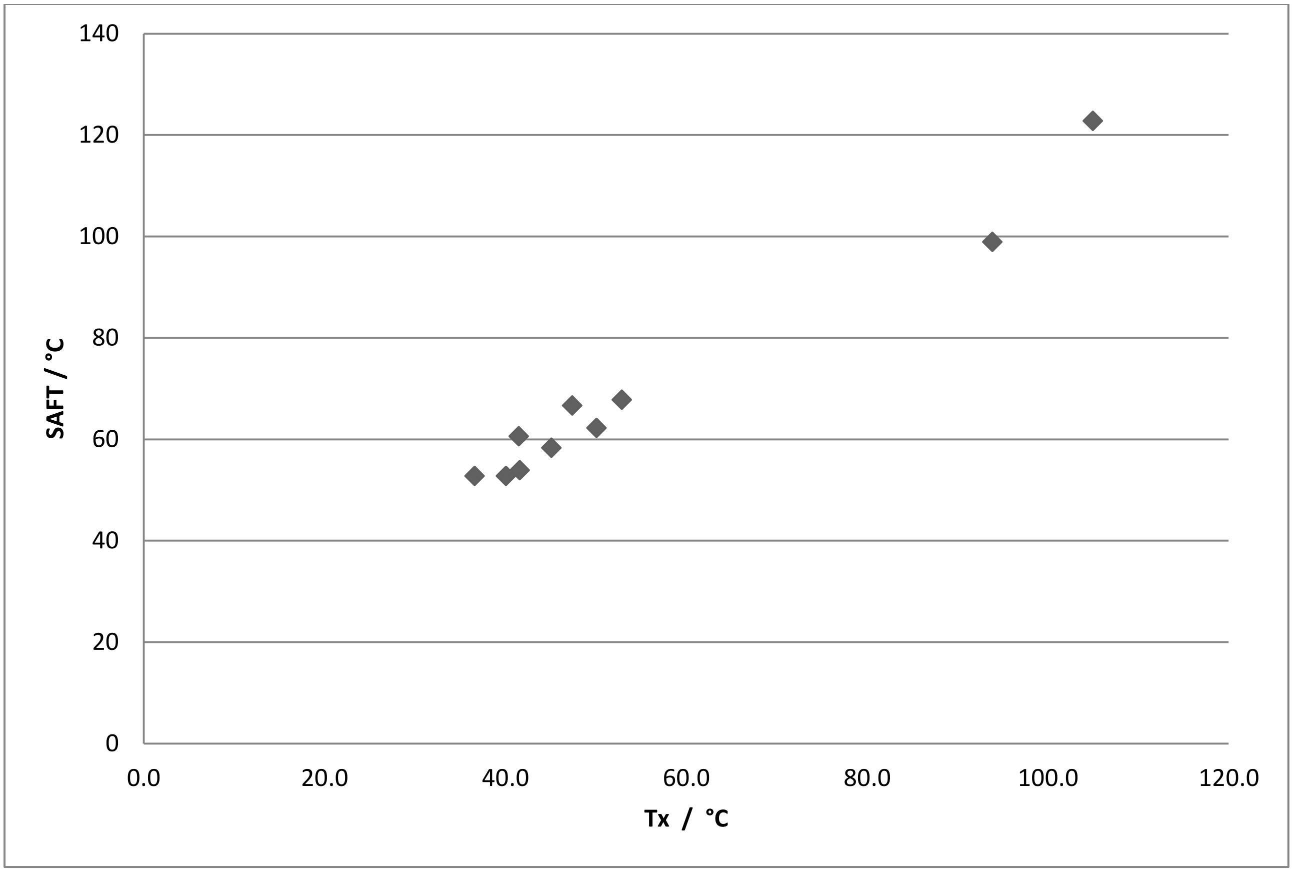

Figure 4. Dependence of the shear adhesion failure temperature on the cross-over temperature for the same set of adhesives as in Figure 3.

Formulating Adhesives

In contrast to other adhesives, the block copolymer based adhesives undergo no chemical changes during processing, there is no or only insignificant rubber break-down and no cross-linking. The adhesive properties depend only on the formulation. The rheological data allow to determine the potentially best formulations for a given application and screen out unsuitable formulations. For example, a freezer label adhesive must have a low glass transition temperature. All variations with too high a T_g do not need to be tested any further. The sketch in Figure 5 shows how the different components in an adhesive change the rheological curves.

The glass transition temperature can be calculated fairly accurately with the Fox equation:

$$(1) \qquad \frac{1}{T_g} = \sum_i \frac{w_i}{T_{g,i}}$$

w_i are the weight fractions, and $T_{g,i}$ the glass transition temperatures of the components. The inverse of the glass transition temperatures are additive. This means, components with high glass transition temperatures (tackifiers) move T_g to higher temperatures, components with low glass transition temperatures (rubber, plasticizer) move it to lower temperatures. For block copolymers the equation needs to be modified so that the styrene phase is not taken into account.

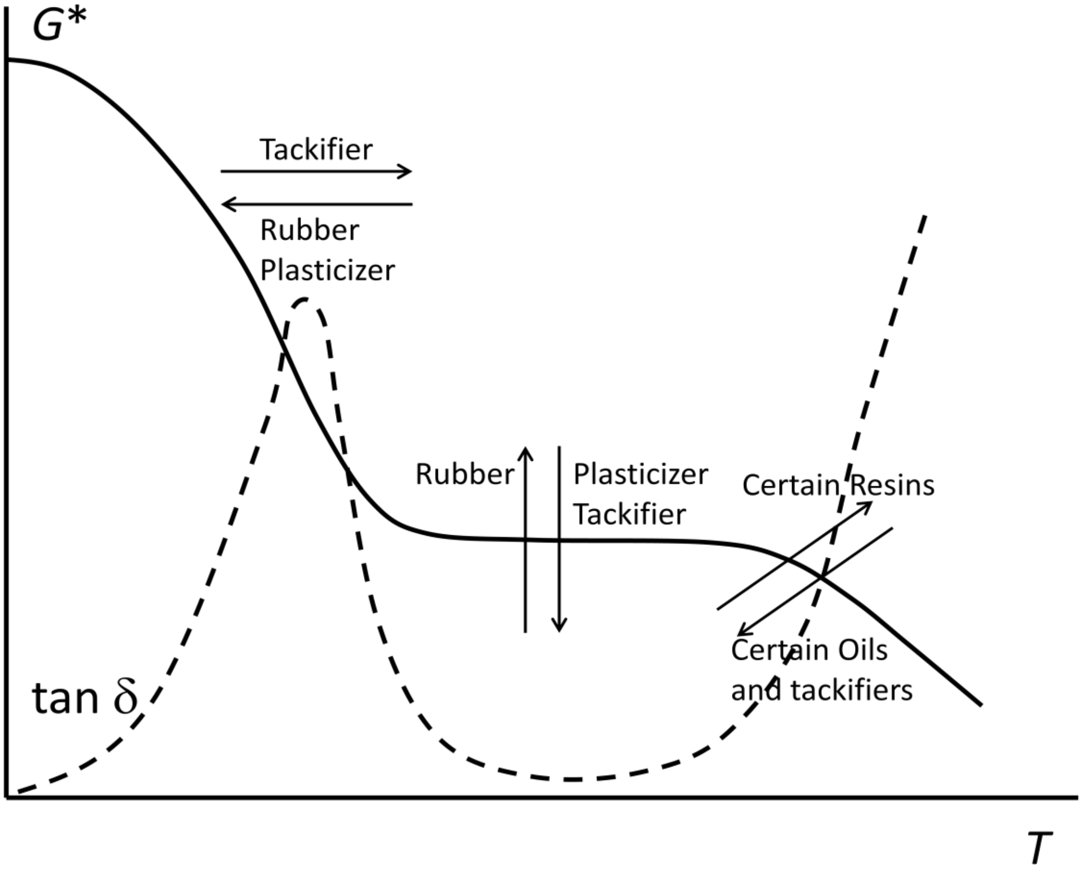

Figure 5: Influence of formulation variations on the modulus and the loss tangent.

The plateau modulus depends on the entanglements and network ties in the isoprene phase. The block copolymer based adhesives will not behave very differently from the polyisoprene homopolymers. Low molecular weight additives, like plasticizers and tackifiers, decrease the polymer concentration and so the modulus decreases. Addition of rubber has the opposite effect.

The softening of the adhesive depends on the glass transition temperatures of the styrene domains. These are very small; their glass transition temperature is lower than that of the homopolymer polystyrene. Most components added to SIS or SBS adhesives are compatible with the isoprene phase and do not change the properties of the styrene phase. Certain oils and tackifiers are miscible with polystyrene and they will also be found in the styrene domains. This will decrease the glass transition temperature of the disperse phase and move the cross-over temperature to lower temperatures. There are some resins that raise the glass transition temperature of the styrene phase. They are added when very good high temperature properties are required. Poly(α-methylstyrene) is an example for such a resin. It has a much higher glass transition temperature than polystyrene and so its addition will raise the glass transition temperature of the styrene phase.

A good way to test if a plasticizer or tackifier will influence the softening is to prepare a 1:1 mixture and perform a temperature sweep. A significant difference between the measured T_g and T_g calculated according to equation (1) indicates that this material does not stay exclusively in the isoprene phase. A considerable change in T_x should be observed in this case as well.

Conclusion

Adhesives based on block copolymers with styrene endblocks and isoprene or butadiene midblocks are microphase separated materials with spherical morphology. This morphology results in thermo-reversible physical networks for triblock or star copolymers giving them excellent cohesive strength. Rheological testing can be used in the product development process to find the most promising formulations, in quality assurance testing for checking the consistency of the adhesive properties, and in competitive testing.

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