

**Society for Adhesion and Adhesives**

## **Hot-Melt Adhesives**

**One-day Symposium 5<sup>th</sup> December, 2002**

**Society of Chemical Industry, Belgrave Square,  
London**

## **Programme**

- 10.00**      **Registration and coffee**
- 10.30**      **Melting and softening of polymers and adhesives**  
**John Comyn, Loughborough University, UK**
- 11.00**      **Nanohybrids as hot-melts**  
**Steve Shaw, QinetiQ Limited, Farnborough, UK**
- 11.30**      **A review of hot-melt adhesives used in the**  
**packaging industry**  
**Peter Bedwell, Sovereign Speciality Chemicals,**  
**Newark, UK**
- 12.00**      **Lunch**
- 14.00**      **A review of hot-melt adhesives used in the**  
**footwear industry**  
**Steve Abbott, SATRA, Kettering and Alan**  
**Herringshaw, Crispin Adhesives, Leicester, UK**
- 14.30**      **UV Curable acrylic hot-melts for pressure-**  
**sensitives**  
**Dr Karl-Heinz Schumacher, BASF AG,**  
**Ludwigshafen, Germany**
- 15.00**      **Recent developments in acrylic/polyurethane**  
**reactive hot-melt adhesives**  
**Andrew Slark, National Starch & Chemical Ltd,**  
**Adhesives Division, Slough, UK**
- 15.30**      **Reactive adhesives utilising “hot-melt” technology**  
**John Bishopp, Star Adhesion Ltd, Cambridge, UK**
- 16.00**      **Discussion**
- 16.15**      **Tea**

This one-day symposium is one of an on going series organised by the Society for Adhesion and Adhesives.

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The next symposium is due to be held at the SCI on Thursday 8<sup>th</sup> May 2003 entitled NDE and Failure Analysis.

Details from

D A Tod  
QinetiQ  
CET/X50  
Fort Halstead  
Sevenoaks  
Kent  
TN14 7BP

01959 514492 phone  
01959 516014 fax  
[datod@qinetiq.com](mailto:datod@qinetiq.com) e-mail

Steve	Abbott	SATRA
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## MELTING AND SOFTENING OF POLYMERS AND ADHESIVES

John Comyn, IPTME, Loughborough University

Hot melt adhesives consist of polymers plus a number of additives, many of which have an effect on the processes of melting and softening.

What are melting and softening? Here I will take a thermodynamic view of melting, i.e. it is the transformation of a crystalline material into a liquid. Polymers are never wholly crystalline, so in this context melting is a change to the crystalline regions. Hot melt adhesives that might be semi-crystalline include polyamides and EVAs.

### Crystalline melting

The measurement of reliable melting points is not without difficulties. The melting point of rubber depends upon the temperature at which crystallisation had occurred. The melting ranges are about 10° and individual melting points vary between 0 and 30°C. What is happening is that the average sizes of the crystallites depend upon the temperature of crystallisation, and melting point varies with crystallite size.

An approach is to use a slow rate of heating (1-2 K day<sup>-1</sup>). The less stable crystallites will melt first but the liquid they produce will recrystallise to larger, more perfect crystallites. As the temperature is increased further this process will be repeated until the whole sample will consist of large almost perfect crystallites, which will finally melt leaving a liquid polymer.

Melting is an example of a *first order transition*, in which abrupt changes occur in volume, heat and entropy.

The heat of melting of a polymer will vary with its degree of crystallinity. If  $\Delta H_u$  is the heat of fusion of a perfectly crystalline sample of a polymer, then the heat of fusion of a sample of degree of crystallinity  $X_c$  will be :

$$\Delta H_f = X_c \Delta H_u$$

$\Delta H_u$  can be found from the depression of melting points of polymer-diluent mixtures, using the Flory-Huggins theory of polymer solutions. The diluent lowers the chemical potential of the polymer in the liquid phase. The equation is

$$1/T_m - 1/T_m^\circ = (R/\Delta H_u)(V_u/V_1) [v_1 - \chi_1 v_1^2] \quad (2)$$

Here  $T_m^\circ$  and  $T_m$  are melting points of polymer and mixture,  $V_u$  and  $V_1$  are the molar volumes of polymer repeat unit and diluent,  $\chi_1$  is the interaction parameter and  $v_1$  is the volume fraction of diluent.

Some data obtained by using this equation with a number of diluents are shown in Table 1. Strong justification for this equation comes from the constancy of  $\Delta H_u$  with the different diluents.

Table 1 Data obtained from melting points of cellulose tributyrate –diluent mixtures.

Diluent	$\Delta H_u$ (kJ mol <sup>-1</sup> )
Tributylin	11.7
Benzophenone	12.1
Hydroquinonemonomethylether	11.7
Dimethyl phthalate	11.7
Ethyl benzoate	13.4
Ethyl laurate	

End-groups, comonomer units and crystal surfaces act as diluents and hence depress melting points. With hot melt adhesives tackifiers and comonomers are obvious diluents.

### Crystallite size

The free energy of fusion can be thought of as having two components thus:

$$\Delta G_t = \Delta G_u + \Delta G_s$$

If the surface free energy per unit area of crystallite is  $\gamma$  and the total surface area is  $A$  then:

$$\Delta G_s = -\gamma A$$

This leads to

$$T_m = (\Delta H_u - \gamma A) / \Delta S_u$$

### Values of $\Delta H_u$ and $\Delta S_u$ and $T_m^\circ$

Some values of these parameters are collected in Table 2. Some correlation in the data are noted below.

(1) The melting point of poly (*trans*-1,4- isoprene) is higher than for poly (*cis*-1,4- isoprene). Differences in both  $\Delta H_u$  and  $\Delta S_u$  contribute. The chains of the *cis*-isomer are more flexible so increasing the entropy of fusion.

(2) Cellulosics have high melting points on account of their low entropies of fusion. Cellulosic molecules are known to be fairly inflexible in solution, and so in melting the number of configurations open to a cellulosic molecule is limited. Molecules which are flexible in the melt would be expected to have high entropies of fusion.

(3) Comparison of polyethylene and PTFE indicates that  $\Delta H_u$  is the parameter which gives PTFE a higher melting point.

(4) Perhaps surprisingly PEO has a lower  $T_m$  than polyethylene. Possibly we would expect the polar ether linkage to increase intermolecular forces and thus increase  $\Delta H_u$  ( which it doubles) and by dipole-dipole interaction to stiffen the PEG molecule and lower  $\Delta S_u$ . Both these effects would tend to increase  $T_m$ . What seems to happen

though is that the -O- group reduces steric hindrance and increases the flexibility of the PEO molecule.

(5) Aromaticity has a chain stiffening effect which lowers  $\Delta S_u$  and increases  $T_m$  (e.g. polyethylene terephthalate and polyethylene adipate).

Table 2. Selected data on polymer fusion.

Polymer	$T_m$ (°C)	$\Delta H_u$ (kJ mol <sup>-1</sup> )	$\Delta S_u$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Polyethylene (linear)	137.5	4.01 ± 0.12	9.77
Poly( <i>trans</i> -1,4-isoprene)	74	12.72	3.66
Poly( <i>cis</i> -1,4-isoprene)	28	4.39	14.58
Isotactic PMMA	160		
Syndiotactic PMMA	200		
Cellulose tributyrate	207	12.55	2.61
Cellulose tricaprylate	116	12.97	3.33
Polyethylene oxide	66	8.28	24.4
PTFE	327	5.73	9.55
Nylon 11	182		
N-Methylnylon 11	60		
Polyethylene terephthalate	265		
Polyethylene adipate	50		

### **Polyamide hot melts**

The polyamide terpolymers 6,6-6,6-10, 6,6-6,12 6,6-6,6-12 and 6,6-9,6-12 are used for bonding textile fabrics, where they are softened by steam, but this facility also lowers their wash resistance. They have good dry cleaning resistance.

The melting points of polyamides are dominated by the ability of amide groups to form hydrogen bonds. Melting point does not change smoothly as the number of methylene groups increases, and polymers with even numbers of carbon atoms are at the peaks of the zig-zag (Figure 1). The molecules lie in sheets with intermolecular hydrogen bonding between -NH- and >C=O groups (Figure 2). The heat of hydrogen bonding contributes to the heat of fusion.

The asymptotic limit of the polyamide melting point, as the numbers of methylene groups become large, is the melting point of linear polyethylene (137°C). This type of behaviour is also shown by aliphatic polyesters and polyurethanes (Figure 3), both of which are used as hot melt adhesives. The use of mixed monomers in polyamide hot melts increases disorder, so lowering the extent of hydrogen bonding and melting point.

### **Softening**

Polymers exhibit stress relaxation, due to their viscous components. Plots of stress relaxation modulus against temperature for linear amorphous polymers are of similar shape (Figure 4) and fit the Williams-Landel-Ferry equation.

$$\log a_T = \frac{-17.44 (T - T_g)}{51.6 + (T - T_g)}$$

Here  $a_T$  is a shift factor and hence  $T_g$  is the glass transition temperature.

There are four regions of viscoelastic behaviour, which are glass, glass transition, rubber and melt.

### Viscous flow

The viscosity of a molten polymer falls as the shear rate rises, because shearing tends to make the chains align. Melt viscosity increases with molar mass. At low shear rates and lower molar masses, plots of  $\log$  (viscosity) against  $\log$  (molar mass) are linear and of slope 1.7. Above a critical molar mass ( $M_c$ ) the slope increases to 3.4 (Figure 5). There is a kink at a critical molar mass, due to the formation of entanglements. Some values appear in Table 3.

Table 3. Values of  $M_c$  from  $\log \eta_0 - \log M$  plots

Polymer	$M_c$
Polyethylene	3800
Polyvinyl acetate	24500
Polydimethylsiloxane	24400
Polystyrene	36000
Poly(1,4-butadiene)	5000
Polyisobutene	15800

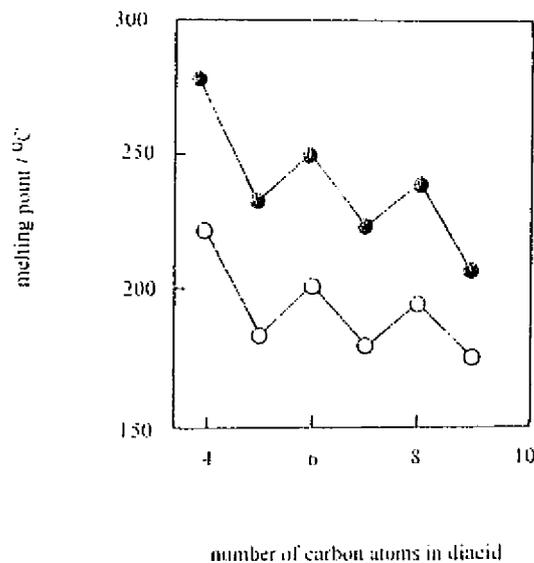


Figure 1. Melting points of polyamides based on tetramethylene diamine ● and pentamethylene diamine ○.

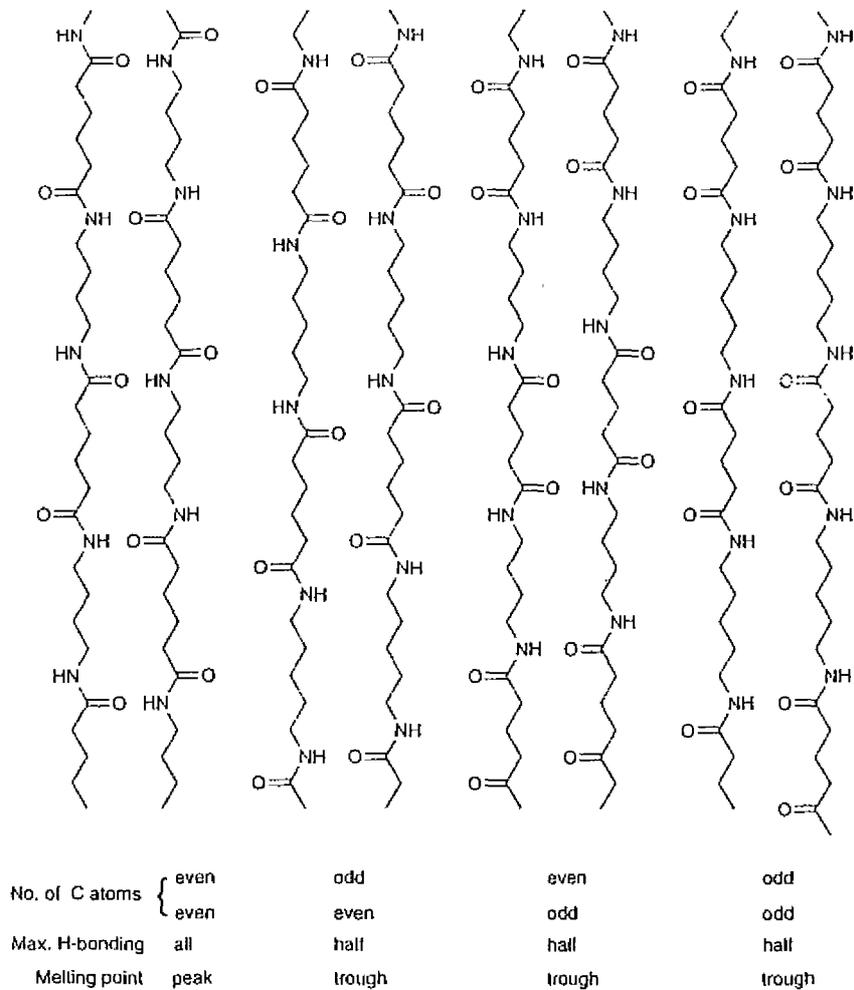


Figure 2. Hydrogen bonding in polyamides made from diacids and diamines.

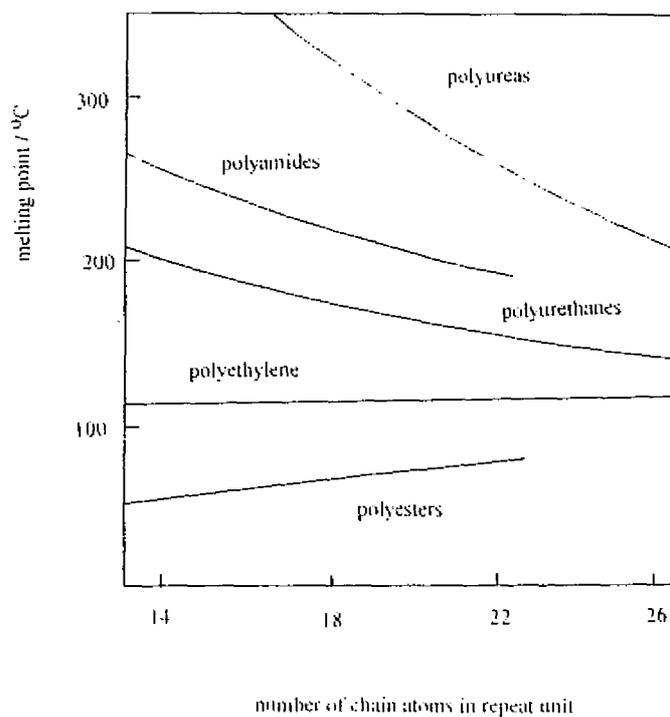


Figure 3. Smoothed melting points of linear aliphatic polymers.

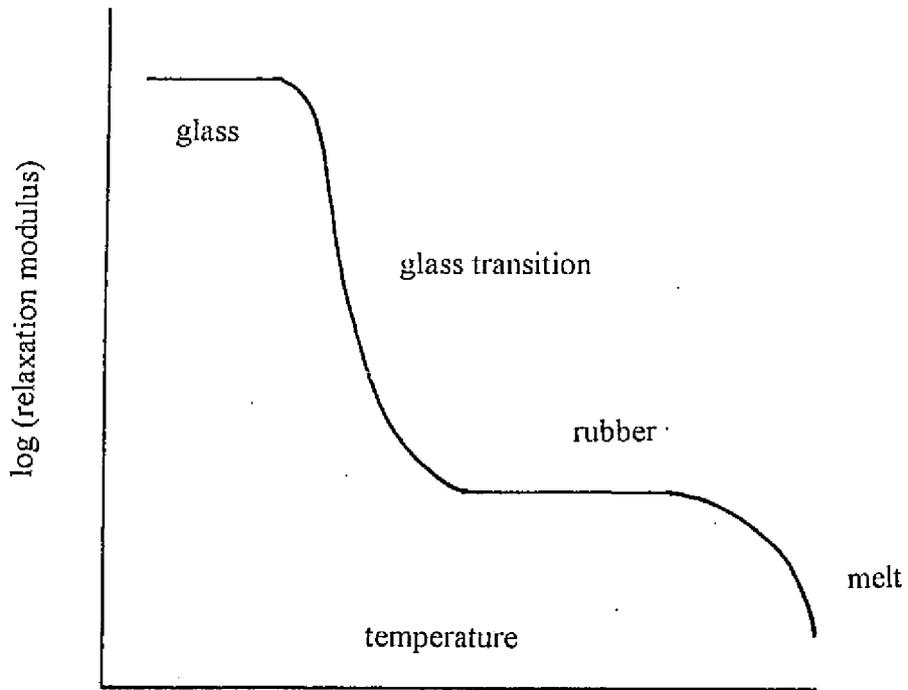


Figure 4. Dependence of relaxation modulus on temperature for a linear amorphous polymer.

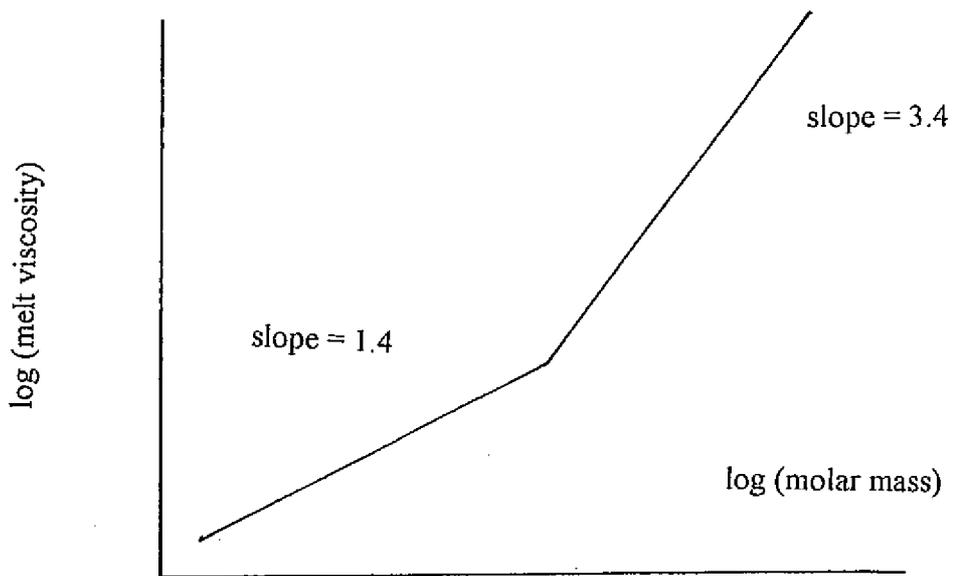


Figure 5. Dependence of melt viscosity on molecular weight for a linear polymer.

## A REVIEW OF HOT MELT ADHESIVES USED IN THE FOOTWEAR INDUSTRY

S G Abbott, SATRA Technology Centre Ltd, Kettering  
A Herringshaw, Crispin Adhesives Ltd, Leicester

The footwear industry makes extensive use of adhesives, appreciating their ability to join dissimilar materials and produce unobtrusive flexible joints. Hot melt adhesives facilitate rapid bonding processes and have been adopted for a range of assembly operations, supplanting solvent-borne or latex adhesives and mechanical fastenings. The processes suited to hot melts mainly concern assembly of components of the shoe upper prepared from leather, textile and board materials. The demanding task of attaching the upper to the polymer-based sole has so far seen little use of hot melt adhesives, for reasons which will be outlined.

### **Adhesive applications**

#### *Laminating*

Polyamide or styrene-butadiene-styrene thermoplastic rubber (SBS) hot melt adhesives are used to laminate materials for shoe uppers and to combine upper components to linings. The adhesive is applied by a heated roller, usually with a gravure surface to produce a discontinuous dot coating, or by a fibre-forming technique to give a fine web. The aim is to produce adequate bonding without significant reduction in the 'breathability' of the materials.

The materials are either combined immediately, or in subsequent processes which use a heated press or roller to reactivate the cooled adhesive. Sometimes components are temporarily joined, using adhesive from a hot melt gun, prior to sewing.

#### *Folding*

The edge of the upper which is top-most in the finished shoe, known as the 'top-line', is chamfered and folded to produce a smooth surface and a neat appearance. The folding machine applies polyamide hot melt adhesive to the edge of the component and the fold is secured by a hammer action.

#### *Bonding stiffeners*

Stiffeners are inserted at the heel area of the upper and at the toe ('toe puff') to maintain the shoe shape. The most common stiffener material comprises non-woven fabric impregnated with a thermoplastic resin such as a styrene copolymer, with a surface coating of ethylene vinyl acetate (EVA) hot melt adhesive. The stiffener is laminated to the corresponding upper component in a heated press. Before the completed upper is shaped around the last the adhesive and stiffener are softened, using a heated press, clamp or steam conditioning unit.

#### *Lasting*

Of the operations in which hot melt adhesives are widely used this is the most critical. The shoe upper is stretched around the last (the former on which a shoe is built) and its edge secured to the insole. The insole is usually cellulose board, comprising cellulose fibres and a rubbery binder, or a non-woven type based on synthetic fibres with a polymeric impregnant.

Once done manually with pincers, hammer and tacks, pulling and securing the upper is now the province of sophisticated lasting machines. These apply hot melt adhesive from a heated nozzle immediately before the upper material is pulled over and flattened onto the insole. The

adhesive must have good initial grab and quick setting properties, the bond consolidation taking only 1-2 seconds.

Polyester adhesives are used at the forepart of the shoe as they are quick setting and will hold the complex pleating of the upper material. They are also relatively brittle and give little clogging of the abrasive paper used to flatten and abrade the upper material for attachment of the sole. At the side or waist of the shoe polyamides are preferred, being more flexible and giving better wetting out of the materials. Higher softening point polyamides can also be used at the forepart.

#### *Shank insertion*

The shank, a metal or wooden reinforcing strip which stiffens the shoe in the instep region, is often attached to the insole of the lasted shoe with blobs of polyamide or EVA hot melt. This is effectively a temporary attachment as the shank is later sandwiched between the insole and the sole.

#### *Sole attaching*

Bonding the sole to the lasted upper of the shoe is the most demanding adhesive application in footwear, requiring a peel strength of around 5 N/mm compared with 0.3-1 N/mm for the other operations described. Conventional hot melt adhesives have seen only limited commercial use for this task and have not proved suitable due to their relatively high viscosity and poor wetting of substrates such as leather.

Since the 1980s a number of efforts have been made to use hot melts based on reactive polyurethanes. The adhesive as applied has a relatively low molecular weight and viscosity, but on setting gives an adequate initial bond strength. The adhesive then cures and crosslinks in the joint due to the action of the moisture inherent in shoe materials, giving a higher ultimate bond strength. Despite successful trials the process has seen only spasmodic use, due to concerns at adhesion problems with some materials, the need for tight process control, and above all the sophisticated application machinery which is required.

#### **Adhesives and processing**

The polyamides used in footwear are condensation products of dimer acids, derived from castor oil or tall oil, with diamines. They are not crystalline, unlike the polyesters which are of the terephthalate type. Both adhesives have sharp melt/viscosity characteristics, and are fast setting compared with other types such as EVA.

Typical application temperatures are: polyamide (folding) 130-170°C, polyamide (lasting) 170-240°C, polyester 200-240°C, EVA 100-190°C, SBS 100-150°C. In each case the softening point is 20-25°C lower.

Adhesives are usually supplied in granule or rod form, the latter mostly as a continuous reel for automatic machine feed.

On prolonged heating polyamides darken, thicken and skin, whereas polyesters thin to a lower viscosity. Modern machinery melts the adhesive on demand so heat stability problems are now uncommon.

Polyamides and polyesters bond most materials satisfactorily and are reasonably tolerant of leather grease. When bonding problems occur these are generally associated with incorrect

application or reactivation temperature, or an inadequate amount of adhesive. The adhesive softening point must be sufficient for bonded joints to withstand heat in subsequent shoemaking processes. This is particularly important for lasting adhesives, as the newly lasted upper is subjected to a heat-setting process, to maintain the shoe shape when the last is finally removed.

### **Testing**

The softening point of hot melt adhesives can be determined by the 'ring and ball' technique originally developed for petroleum resins. The adhesive is cast into brass rings, and a steel ball bearing placed on the centre of each adhesive layer. The assemblies are heated in a glycerol bath at a constant rate of temperature increase until the adhesive softens sufficiently for the ball to drop through the ring. The corresponding temperature is taken as the softening point.

The heat resistance of a bonded joint can be checked by hanging a loaded shear test specimen in an oven and progressively raising the temperature until failure occurs.

Viscosity can be measured using a viscometer with a heated cell, but a simple but effective technique for comparative purposes also uses ball bearings. Adhesive is heated in a boiling tube to the required temperature, a ball bearing is dropped into the melt, and its time of descent between two marks on the tube is determined. The greater the time, the higher the viscosity.

A challenge with hot melts is preparing test specimens for performance tests under realistic conditions. With pre-applied adhesive coatings this is not too difficult, a heated platen press or heat reactivator can be used to melt the adhesive. Adhesive applied as a molten ribbon immediately before joint closure presents problems of speed of working. Experience at SATRA showed that a test specimen comprising insole board and upper leather could be bonded simply and effectively by applying adhesive from a heated pot or gun onto one adherend, then bringing the second adherend into place and consolidating the joint. Unfortunately, peel tests mostly showed interfacial failure at the adherend surface to which adhesive had not been applied – in other words the adhesive was too cool by the time this surface made contact!

To overcome this problem a roller press was devised with a means of supporting a peel test specimen, stapled at one end and held open, close to the roller nip line. A trigger mechanism enables the test specimen to be fed into the rollers immediately adhesive is applied from a gun to the open joint. This equipment produces bonded joints which behave similarly to sections cut from a shoe.

The peel test is used to check the performance of hot melt adhesives in bonding footwear materials. For most applications requirements are undemanding, but for lasting adhesives a peel strength of 1-1.5 N/mm is typical, accompanied by surface failure of one of the materials. Joints to cellulose boards show a directional effect due to the orientation of the fibres.

### **Conclusions**

Footwear manufacture provides a good illustration of the versatility of hot melt adhesives for rapid assembly, and their suitability for all but the most demanding applications.

# UV-CURABLE ACRYLIC HOTMELTS FOR PRESSURE SENSITIVE ADHESIVES

Dr. Karl-Heinz Schumacher, BASF AG  
Ludwigshafen, Germany

## 1. SIS/SBS-HOTMELTS FOR PRESSURE SENSITIVE ADHESIVES

Today three types of adhesive raw materials are used for pressure sensitive adhesives, solvent-borne acrylics and rubbers, aqueous dispersions and SIS/SBS-block-copolymer hotmelts. Among these the SIS/SBS-hotmelts show the strongest growth rates. There are two basic factors for the market success of the SIS/SBS-hotmelts:

- Aggressive tack and tailor-made peel adhesion by modifying with a large variety of tackifier resins and plasticising agents
- Economic attractiveness due to low costs of the raw materials and the coating technology and due to high production speed even at high coating weights

Although the introduction of SIS/SBS-hotmelts is a real success story, there are some basic disadvantages of this type of raw material, which prevent them from being used for still a greater number of applications:

- Poor aging behavior (yellowing and embrittling) caused by oxidation of residual double bonds in the polymer
- Low film transparency does not allow production of crystal clear self adhesive labels and tapes
- Moderate heat resistance

The established alternatives for those applications, for which the use of SIS/SBS-hotmelts is not possible, are solvent- or water-borne adhesives. The preferred type of polymer being used for those types of adhesive raw materials are the acrylics, because they guarantee an excellent aging behavior and an optimum visual appearance. However, also these alternatives have specific disadvantages that limit their attractiveness, e.g., the ecological and toxicological risks of solvent-borne adhesives and the moderate water resistance of water-borne adhesives. And there is the fact that for both of the alternatives only slow production speeds are possible, especially at high coating weights, due to the necessary evaporation of organic solvent or water.

Considering these disadvantages of the established systems our goal was to develop a new class of adhesive raw material for self adhesive articles that combines the attractive coating technology of the SIS/SBS-hotmelts with the excellent visual appearance and heat resistance of the solvent- or water-borne acrylics.

## 2. acResin® UV – COMBINING HOTMELT COATING TECHNOLOGY WITH HIGH PERFORMANCE ACRYLIC CHEMISTRY

### 2.1. Chemistry of acResin UV

The acResin UV products consist of acrylic copolymers that include copolymerised photoreactive groups. To make acResin UV coatable on carriers like paper or foils at reasonable temperatures the molecular weight of the polymer is limited to about 200 000 g/mol. To produce an adhesive with a substantial cohesion the coated acResin raw material has to get a much higher molecular weight. This is achieved by UV irradiation. Under the action of the UV-light the photoreactive groups in acResin UV crosslink the acrylic polymer backbone molecules by a chemical grafting reaction.

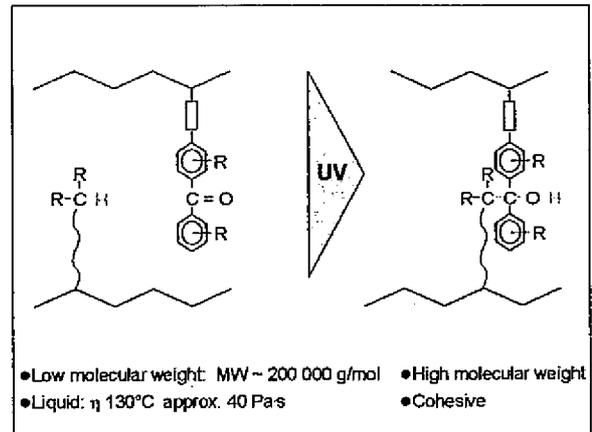


Fig. 1: Principle of acResin UV

This chemical principle of acResin UV is basically different from other types of UV-acrylics. Whereas acResin is already a polymeric raw material which achieves an additional crosslinking by UV light, other UV acrylics being used as adhesive raw materials consist of mixtures of oligomers with monomers and photoinitiators. Such mixtures react after being coated onto the carrier in a real radical polymerization of double bonds. That other type of UV-acrylic has also been introduced into the adhesive market. However, its disadvantages like the unpleasant odor and toxicity risks arising from residues of monomers and the photoinitiator, the low coating speed and the fact that an

incristation with nitrogen is necessary have restricted the market success of that system so far.

## 2.2. Processing acResin UV

acResin UV can be processed with standard equipment for SIS/SBS-hotmelts that may already be available in a production site for self adhesive articles. The remaining required investment is the modification of the machine with UV-lamps.

To coat acResin on the carrier the adhesive has to be heated up to 100 – 140 °C. In this temperature range acResin UV becomes liquid enough to be coatable with common slot-die or roll systems.

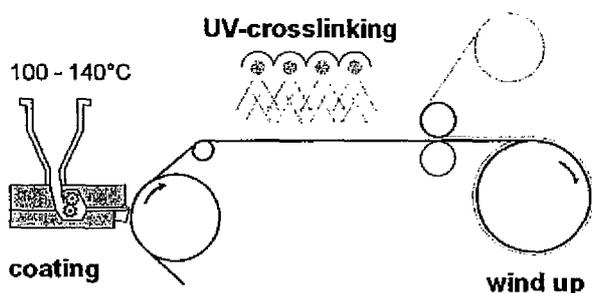


Fig. 2: Processing acResin UV

Standard mercury medium pressure bulbs as known from other applications are typically used as the light source.

## 2.3. Crosslinking Mechanism of acResin UV

To achieve an efficient crosslinking of the acResin UV molecules UV-light with a special wave length band is needed, as the UV-light has to match with the UV-absorption of the photoreactive groups in acResin UV. A closer look at the crosslinking mechanism of acResin UV reveals that the concentration of the triplet radical T1 in the carbonylic function of the benzophenone group is responsible for the resulting crosslinking efficiency. Hence, the higher the T1 radical concentration, the more photoreactive groups will react and the higher the resulting crosslinking density will be.

Only UV-irradiation in the UV C- band between 220 and 280 nm is decisive for the formation of the triplet radicals T1. Therefore, only the UV emission peaks in this range contribute to the crosslinking of acResin UV. Common medium-pressure mercury

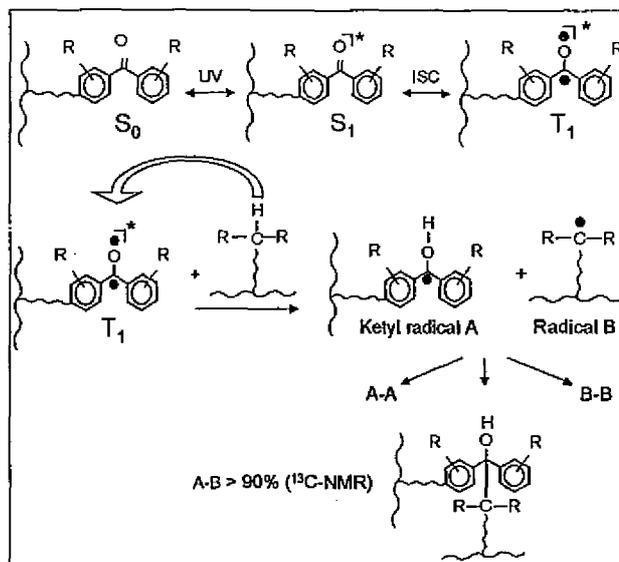


Fig. 3: Crosslinking mechanism of acResin UV

vapor lamps emit UV irradiation with the correct wave lengths and therefore are well suited.

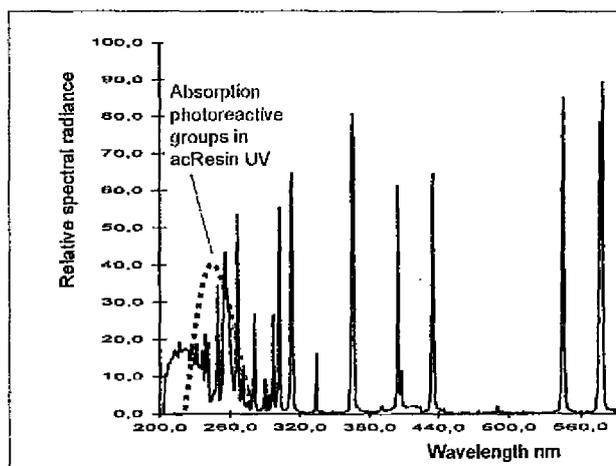


Fig. 4: UV emission of a standard UV-lamp

## 3. TAILORING THE ADHESION PROPERTIES BY THE UV-DOSE

A special feature of acResin UV is that the adhesive properties can be tailored by adjusting the UV C-dose to which the coated adhesive is exposed. The higher the UV-C dose, the higher the cohesion and the lower the adhesion. This is a consequence of the crosslinking density and makes it possible to produce a whole

range of different articles from one raw material just by modifying the UV C-dose.

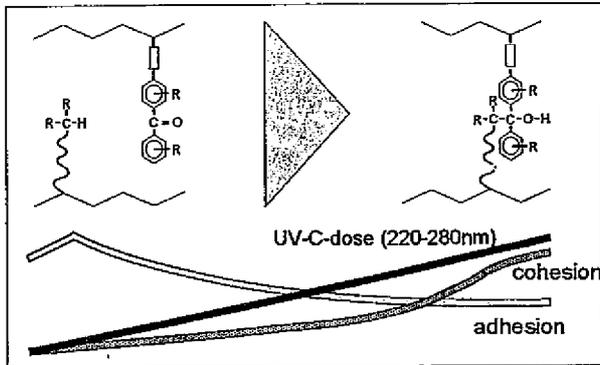


Fig. 5: Tailoring the adhesives properties by the UV-dose

For example, acResin DS 3532 is an adhesive raw material, which is well suitable for two completely different applications. Being crosslinked with a low UV-dose, acResin DS 3532 is a good adhesive for deep freeze labels, whereas a crosslinking with high UV-doses produces an excellent adhesive for removable labels.

### 3.1. acResin DS 3532 for Deep-Freeze Labels

A UV C-dose of 3 - 5 mJ/cm<sup>2</sup>, measured with the UV Power Puck<sup>®</sup>, produces an only slightly crosslinked adhesive with an attractive tack even at very low temperatures. Although the glass transition temperature of the polymer is very low (-60°C), the crosslinking level is already high enough to produce a cohesion of the adhesive being sufficient to cut and stamp laminate rolls without any edge bleeding problems.

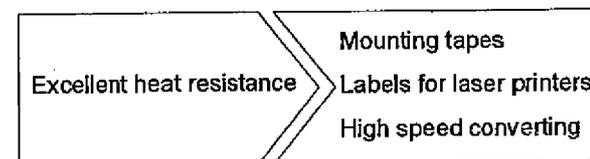
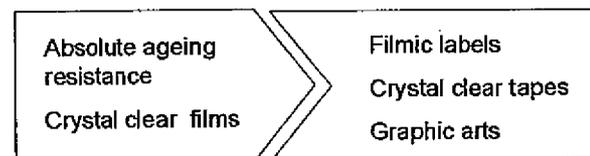
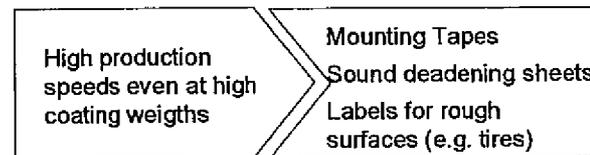
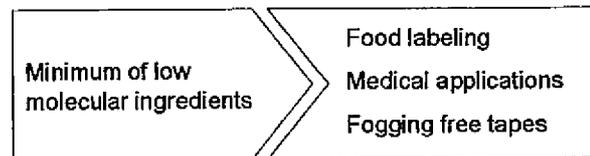
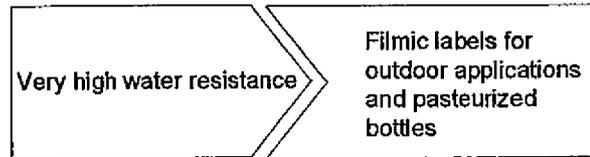
To obtain significant higher quickstick and peel values in the temperature range of -10 - 30 °C acResin DS 3532 can be mixed with hydrocarbon tackifier resins, which do not absorb in the UV-C wave length band, e.g. with Regalite<sup>®</sup> R-9100.

### 3.2. acResin DS 3532 for Removable Labels

Crosslinking acResin DS 3532 with a UV C-dose of 20 - 25 mJ/cm<sup>2</sup> produces a much more cohesive, less tacky adhesive. Labels being coated with such a product show excellent peel values and can be removed after use from a wide variety of different surfaces without leaving any visible residues.

## 4. BENEFITS OF acResin UV

Besides the fact, that a whole range of different articles can be produced from one raw material by adjusting the UV-dose, acResin UV offers many other advantages. These benefits predestine acResin UV for a large number of very interesting applications. The benefits and recommended applications may be summarized as follows:



The commercially available product range comprises four products. acResin DS 3532 for deep-freeze and removable labels was discussed in chapter 3. acResin A 203 UV has been developed for applications, in which a formulation with tackifier resins is necessary.

This is true for most of the label applications. acResin A 258 UV and DS 3552 are the UV acrylic hotmelts for non-formulated applications. Here the focus is self adhesive tapes. acResin A 258 UV can be used for coating weights up to 100 g/m<sup>2</sup>, acResin DS 3552 up to 130 g/m<sup>2</sup>.

## RECENT DEVELOPMENTS IN ACRYLIC/POLYURETHANE REACTIVE HOT MELT (RHM) ADHESIVES

Dr. Andrew T. Slark

National Starch & Chemical Ltd, Adhesives Division,  
Wexham Road, Slough, Berkshire, SL2 5DS, UK

Tel: +44 (0)1753 501301 e-mail: [andrew.slark@nstarch.com](mailto:andrew.slark@nstarch.com)

### Acrylic/polyurethane RHM technology

Moisture curable polyurethane reactive hot melt adhesives are synthesised by the reaction of diisocyanates with diols in the melt, typically at temperatures above 100 °C and under vacuum in the absence of moisture. The reaction is a classic step-growth polymerisation, where molecular weight is controlled by the extent of reaction, functional group stoichiometry and impurities. Typically, the diisocyanate is used in excess to both control molecular weight and ensure that the materials produced contain moisture curable isocyanate end-groups.

There are a number of physical properties that are key to performance. The melt viscosity and rheology of the adhesives are very important in controlling their application. Of particular importance is melt stability and it is desirable that melt viscosity and rheology do not change significantly during dwell time on application equipment. The adhesive should provide good wetting, the appropriate open time and adequate "green" (uncured) strength during the first hour after bonding. Moisture from the atmosphere and substrates diffuse into the adhesive causing chemical changes to occur:

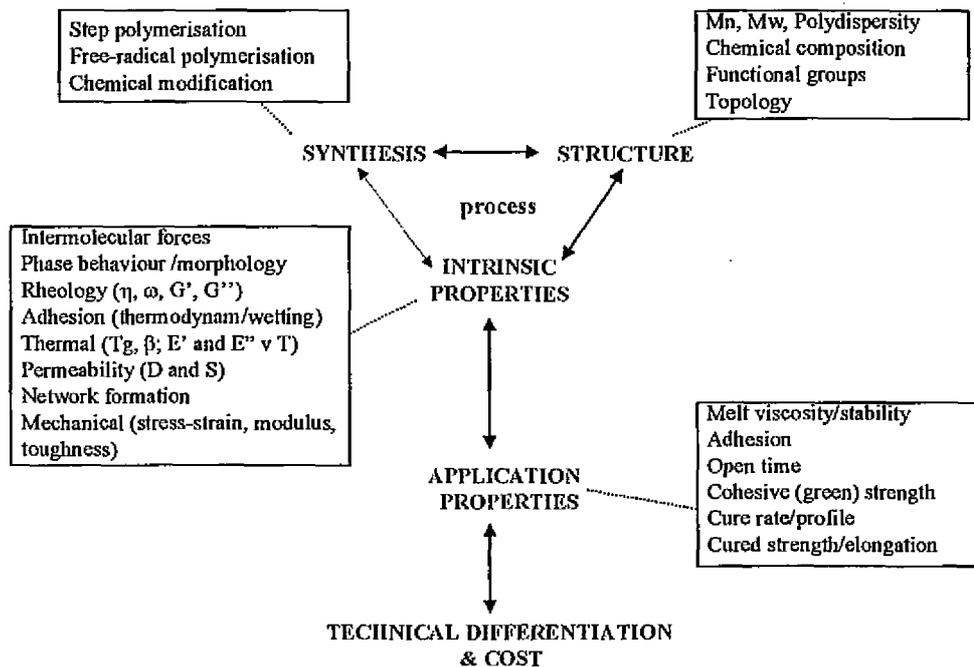
1. Conversion of isocyanate to amine.
2. Chain extension by reaction of isocyanate with amine to produce urea.
3. Branching reaction of isocyanate with urethane to produce allophanate and isocyanate with urea to produce biuret.

The latter leads to a crosslinked product and the final properties of the bonded assembly depend on the structure of the crosslinked network, influenced by the functionality and architecture of the prepolymers. Polyurethane reactive hot melts find application in, e.g. packaging and converting, textiles, automotive, woodworking and a variety of building components, some of which can be classified as approaching semi-structural.

A wide range of adhesives is possible from the plethora of raw materials that are currently available. Polyether polyols such as poly(propylene glycol) are available in a range of molecular weights. These materials behave as good diluents, impart flexibility and are relatively inexpensive. A wide range of polyester polyols is available, varying from amorphous liquids to semi-crystalline solids in a variety of molecular weights; the choice of polyester has a marked influence on adhesive properties. National Starch has a leading position in acrylic modified polyurethane reactive hot melt adhesives. Methacrylate based copolymers made from free-radical polymerisation are dissolved in the polyol mixture before reaction with diisocyanate. Some of the acrylic materials contain pendant functional groups that also react with the diisocyanates. This technology provides a good balance of properties, especially producing low melt viscosity, long open time and good green strength.

## Superior products via a scientific approach

Providing major differentiation of key applied adhesive properties requires an understanding of the intrinsic, basic properties of these material assemblies and how this is influenced by molecular structure. An overview of the link between synthesis, molecular structure, basic properties and applied adhesive properties is shown below. Various synthetic techniques (*synthesis*) are used to produce polymers and prepolymers with different architectures (*structure*). Different polymer structures are combined in a RHM adhesive material assembly to produce a variety of basic properties (*intrinsic properties*) that correlate to adhesive performance in the end-use (*application properties*).

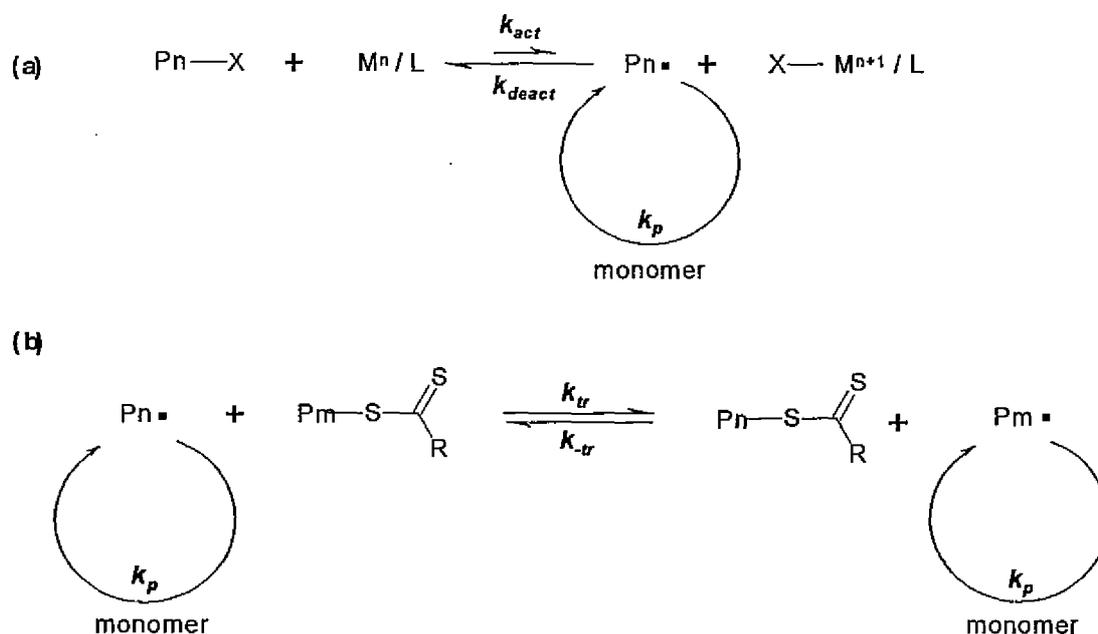


It is important to develop the key, quantitative relationships between application properties and intrinsic, basic properties of the material assemblies that promote major technical differentiation. This information is crucial to drive the effective design of those molecular features that produce optimum performance via the material assembly. Examples will be shown where various analytical tools (GPC, NMR, MALDI, IR, MDSC, DMTA and rheology) have been used to characterise structure & intrinsic properties in comparison with application performance.

## New technology for functional prepolymers

Precise control of free-radical polymerisation has been considered difficult for a long time because of the high reactivity and low selectivity of the growing radical species. Excellent progress has been made in the last 15 years, since several new technologies have been developed which are aimed at precisely controlling free-radical polymerisation of styrenics, methacrylates and acrylates. In chronological order, these are nitroxides (mid 1980's), Atom Transfer Radical Polymerisation (ATRP, mid 1990's - (a) below) and Reversible Addition Fragmentation

Transfer (RAFT, 1998 - (b) below). Nitroxides and ATRP are based on the reversible formation of reactive propagating radicals from dormant covalent species.



In principle, polymers of a wide molecular weight range with a narrow molecular weight distribution can be made. Using appropriately functionalised macroinitiators, it is also possible to produce controlled block copolymers, graft copolymers, star copolymers and branched copolymers. In order to be exploited, an enhanced understanding of the physical properties that these controlled materials confer must be achieved. In addition, the techniques need to be proven as robust in industrial environments, so that the facile nature of conventional free-radical polymerisation is retained.

The extreme control offered by these methodologies could be proven unnecessary and adhesive applications could be satisfied by pragmatic modification of polymer architecture. Improvements over conventional free-radical polymerisation will be possible, providing new structures that have some heterogeneity. These will be significant improvements over those architectures currently available and they could provide a step-change in property enhancements. All of this is likely to be achieved in a cost-effective manner, with all the advantages of current conventional radical polymerisation.

### Changing the game via novel material assemblies

While being versatile, the current toolkit that is used to produce adhesive material assemblies does have limitations. NSC Adhesives is proactively working on new technology to change the current paradigms of performance in order to both revolutionise the use of reactive hot melts in current applications and broaden their use into different market segments. The new technologies include novel moisture curable polyurethanes based on new materials and alternative chemistry to moisture-cured isocyanates. Examples will be shown where step-change improvements are being made to both the intrinsic properties of the adhesive material assemblies and the resulting application properties.

## Reactive adhesives utilising “hot-melt” technology

John Bishopp, Star Adhesion Ltd, Waterbeach, Cambridge, UK

[Presented at the SAA Seminar “Hot-Melt Adhesives” on 5<sup>th</sup> December 2002]

### Introduction

The rheological performance of true hot-melt adhesives is, of all their properties, one of the most important as far as adhesion is concerned.

As their name implies, these adhesives melt under the application of heat. This allows them, on application, readily to flow over the substrate to be bonded, both displacing the air between matrix and adherend and at the same time giving the required intimate contact, through good wetting of the underlying substrate, to maximise adhesion.

However, for reactive adhesives – especially for those deigned for structural applications – a similar degree of intimate contact can, generally, only be achieved by the use of water-based or solvent-based adhesive solutions/suspensions. The former are not easy to formulate and in both instances the solvent medium has to be removed before bonding. This generally means the application of heat and the need to protect the environment from the gaseous evolutions.

Certainly many reactive, structural paste adhesives do exist and by careful control of their rheology a reasonable degree of air displacement and wetting can be achieved. However, these systems tend to be uneconomic in the amount used compared with the actual quantity needed, messy and often they contain raw materials which are hazardous to health: viz. the corrosive nature of many of the hardener components in epoxy-based paste adhesives.

What is needed is a reactive matrix system which is solid at ambient temperatures, will readily melt [without activating the curatives], give a low enough melt viscosity to enable good wetting of the substrate to take place and will then cure. In this case this would be achieved by the application of more heat rather than the removal of the heat source, as happens with true hot-melts.

By careful formulation, this requirement can be met with some reactive systems; but not all. The structural adhesives so produced are generally classed as “Film Adhesives” as they are, more often thannot, supplied as foils [like a sheet of paper or plastic] and can be simply cut to the shape and size of the area to be bonded.

### Reactive Adhesives

A reactive adhesive is a multi-component system which, after application to the adherend, changes its physical form from liquidous to infusible solid by chemical reaction; these polymerisation and cross-linking reactions are often thermally induced.

The chemistries associated with reactive adhesives can be broadly categorised as follows:

- **Acrylics**
  - Anaerobic
  - Conventional Acrylics
  - Cyanoacrylate
  - “Second Generation” Acrylates
  - UV-Activatable/Curing
  
- **Amino-Formaldehyde**
  - Urea-Formaldehyde
  - Melamine-Formaldehyde
  
- **Epoxy**

- **Phenolic**
  - “Phenol-Formaldehyde” Novolac
  - “Phenol-Formaldehyde” Resole
  - Resorcinol-Formaldehyde and R/F-P/F Hybrids
- **Polyimides**
  - Bismaleimide [BMI]
  - Polyimide [PI - e.g. PMR-2]
- **Polyurethanes [PUR]**
- **Silicones**

Of the above generic chemistries, only two readily lend themselves to the formulating techniques associated with film adhesives. These are those based on epoxy and bismaleimide chemistries.

### Formulating Techniques

A typical formulation of an epoxy film adhesive can be generalised as follows; a BMI-based system would be very similar with a BMI backbone rather than an epoxy:

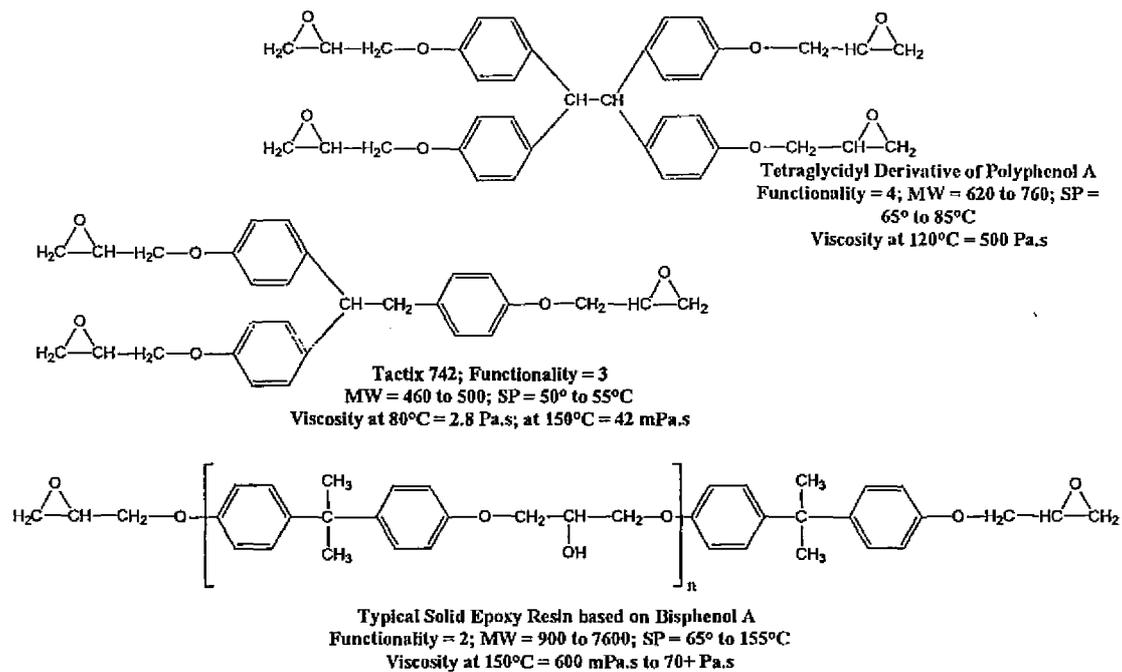
- **Liquid Epoxy Resin**
- **Solid Epoxy Resin**
- **Polymeric Modifier(s)**
- **Hardener**
- **Co-Hardener/Accelerator**
- **Formulation Additive**
  - Flame Retardant
  - Coupling Agent/Surfactant
  - Filler [thixotropic or otherwise]
  - Blowing Agent
- **Pigment/Dyestuff**

However, in transferring “hot-melt” techniques to reactive adhesives it is the choice and loading of only two key raw materials which is really important. These are the solid resin and the polymeric modifier. It is these two materials which turn the otherwise pasty material into a solid matrix which can be produced as a castable film.

Fortunately, the choice of formulating ingredients is large which means that the final matrix can be “tailored”, by the choice of materials with the correct molecular weights, softening/melting points and solubility parameters, to give the required melt viscosity at a temperature below the activation point of the curatives. For example, activation temperatures would be about 80° to 100°C for a urone-accelerated dicyandiamide-cured adhesive and about 150° to 160°C for a conventional dicyandiamide or diamino diphenyl sulphone cure.

**Solid Epoxy Resins:** Not only are the properties such as molecular weight and/or melting point important here but, dependant on the performance required by the bonded structure, the functionality is often key. Thus not only can the correct rheology be “built into” the matrix but properties such as toughness and service temperature can also be successfully modified by the correct choice.

Typical materials are:

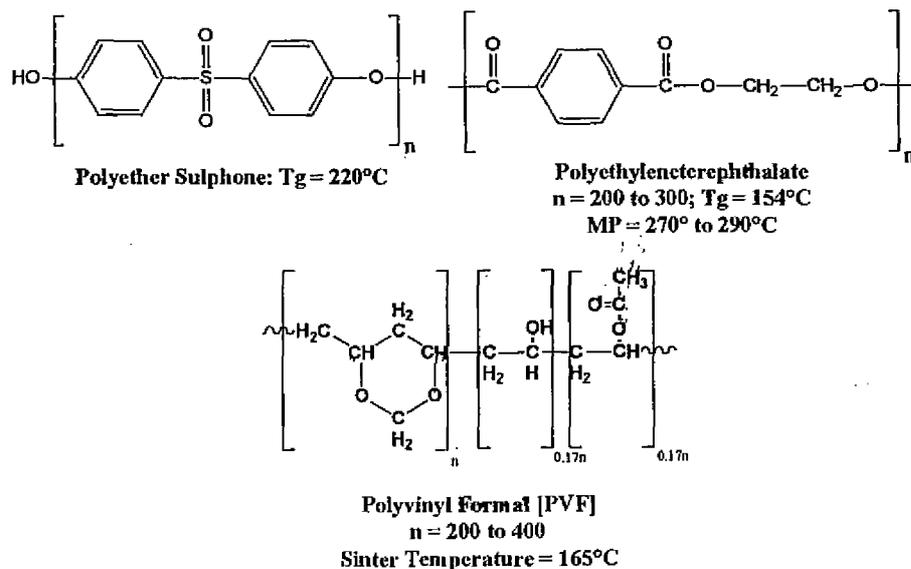


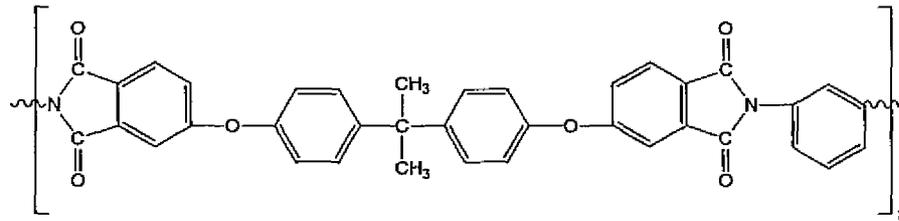
**Figure 1: Typical Solid Epoxy Resins**

All these resins are compatible with conventional liquid epoxies so they can easily be blended to give the required physical properties at both ambient and "melt" temperatures.

**Polymeric Modifiers:** In many cases such a blend, although giving a solid film at room temperature and the required rheological properties at the required temperatures, is relatively brittle and hence difficult to handle. The trick, then, is to incorporate a high molecular weight polymer to give the required handleability; this almost always requires the liquid/solid resin levels to be re-optimised.

As can be seen from the typical structures given below, the typical thermoplastic polymers have very high Tgs; much higher than the activation temperatures of the curatives which will be used. This is where consideration of the solubility parameters of the relevant polymers becomes important. To obtain a true hot-melt resin matrix it is vital that the polymer is soluble in the epoxy resins.



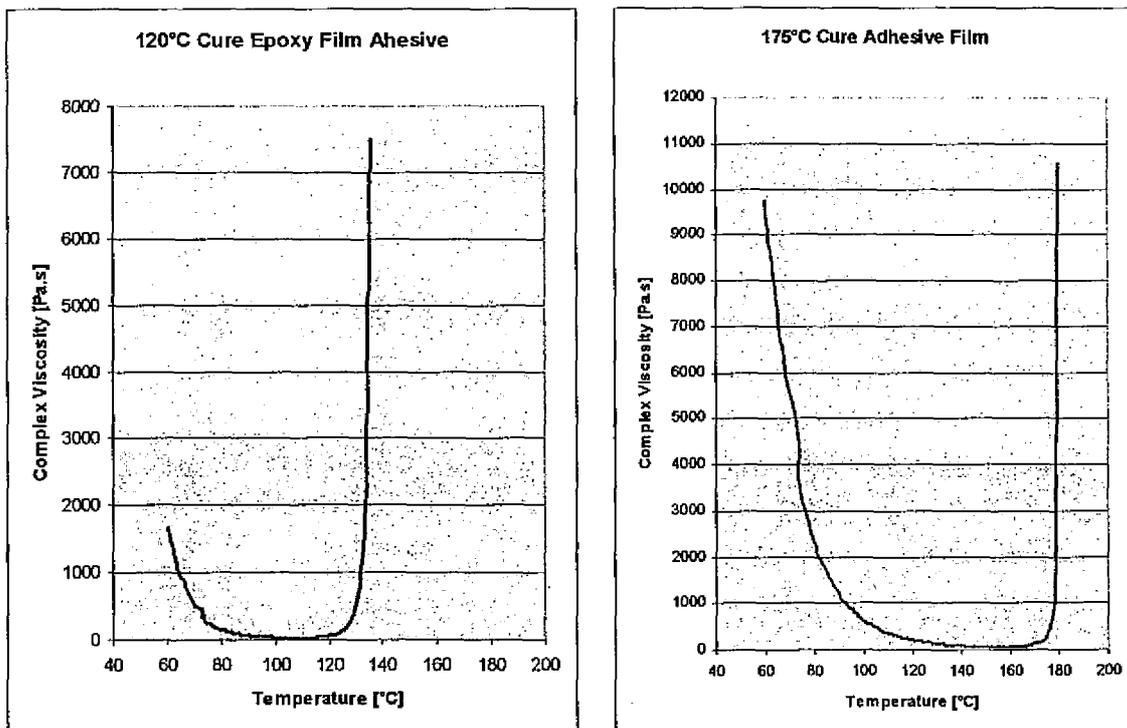


Polyether Imide: Matrimid 5218  
 $n = 15$  to  $27$   
 $T_g = 217^\circ\text{C}$

**Figure 2: Typical Thermoplastic Polymeric Modifiers**

Once the polymer has been dissolved in the resin then the resultant resin matrix can be so formulated as to give a flexible film which can be readily handled at ambient temperatures and will give the required rheological properties at and around a melt temperature which will be below the curative's activation temperature.

Once the matrix formation has been optimised, then the rheological profile should be similar to that shown in the two graphs below. Here it can clearly be seen that each matrix melts rapidly well below its activation point and, most importantly, remains at its minimum viscosity for a significant amount of time to allow the displacement of trapped air and the efficient wetting of the substrate; both essential to obtaining a structural joint.



**Figure 3: Dynamic Viscosity Traces for Two Typical "Hot-Melt", Reactive Film Adhesives**

### Conclusions

Using careful formulating techniques, epoxy [and BMI] adhesive matrices can be produced which initially behave like conventional hot-melt adhesives but then will