

## **Polychloroprene- an evergreen product for the formulation of water based contact adhesives**

Dr. Dieter Gerlach  
Technical Programs Manager  
Du Pont de Nemours International SA  
Geneva, Switzerland

### **Introduction :**

Polychloroprene was the first synthetic polymer to be used by the adhesives industry. The first commercial quantities of this product were available in 1932, and the first grades specifically developed for adhesive application were introduced in the mid-forties. World wide sales of Polychloroprene for use in adhesives are in the order of 50000 tons/year. The principal use of polychloroprene is in solvent based contact cements. This term describes an adhesive which is coated on the surfaces of two substrates and then allowed to dry. Although they exhibit no tackiness after drying, the two surfaces adhere immediately to each other when brought into contact. This instant bond formation allows the end user a fast and easy assembly without the need to clamp.

Main applications for contact adhesives are:

- laminating
- shoe assembly
- automotive interior
- construction
- do-it-yourself

Reason for this behavior is the ability of Polychloroprene to crystallize. The adhesive film is amorphous as long as it contains some solvent and for some time after drying. During this period it has the autoadhesion or contactability. Once the crystallization starts, cohesion develops very rapidly. Although many applications appear fairly basic, demands on the adhesive are often high, such as good contactability, sufficient hot bond strength at temperatures in excess of 100 deg C and long shelf life of the finished adhesive.

### **The solvent issue :**

As long as we disregard the handling of solvents, Solvent based adhesives are very robust and cost effective systems. Their use is simple and they can bond a broad

range of substrates reliably. Due to environmental concerns, regulations on the use of solvents become tighter. There are quantitative limitations on total VOC emissions as well as restrictions on specific solvents such as Toluene or chlorinated solvents. These qualitative limitations often change the characteristics of the adhesive, not only the odour but also more important properties like rheology, drying time, tack and last not least solution stability.

The difficulties associated with the use of solvents increase as we go down the supply chain:

The adhesive manufacturer works in relatively closed systems and should be able to control solvent losses and emissions. He can reclaim solvents and re use them in his process. At the other end, the end user will have to invest heavily in ventilation and solvent recycling if he has to control worker exposure and emissions. This is still technically feasible in an industrial environment but impossible e.g. in the construction industry.

### **the alternatives :**

Systems like hot melt adhesives or liquid reactive adhesives may match the speed of the solvent based adhesive, but will need completely new application technologies, considerable investment and training.

Water based adhesives appear to be a 'natural' choice. They can be applied using basically similar techniques and equipment.

Polychloroprene is made by emulsion polymerization. The latex is an intermediate product in the manufacture of dry Polychloroprene and there is no need to go through the difficult and costly process of converting a solid polymer into a dispersion.

### **Polychloroprene- the product :**

For the better understanding of the product characteristics we will briefly discuss the polymerization process and the parameters which determine the product and subsequently the adhesive properties.

In the emulsion polymerization, free radical initiators are added to an emulsion of monomer, 2-chloro-1,3-butadiene, and surfactants in water. The polymerization is a free radical chain growth mechanism in which monomer molecules are successively added to an active chain end. The submicron polymer particles which form are stabilized by the surfactants in the recipe. The molecular weight is determined by the addition of a chain transfer agent. The polymerization can be taken to full conversion or stopped before. In the latter case, excess monomer is stripped off.

The final product is an aqueous polymer emulsion with low residual monomer levels.

The particle size distribution is broad with a weight-average diameter between 0.1 and 0.4  $\mu\text{m}$ . Surfactants are typically anionic (wood or tall oil rosins). Latex pH is normally high, 12- 13. Total solids range from 47 to 60 %. Depending on solids, surfactants and electrolyte concentration, the viscosity ranges from 45- 600 mPas. There is no relation between the molecular weight of the polymer and the viscosity of the latex.

CR latex can also be produced with non ionic stabilizers: A version based on PVOH is pH neutral. This type of latex is outstanding in shear stability and resistance to heat and electrolytic contaminants.

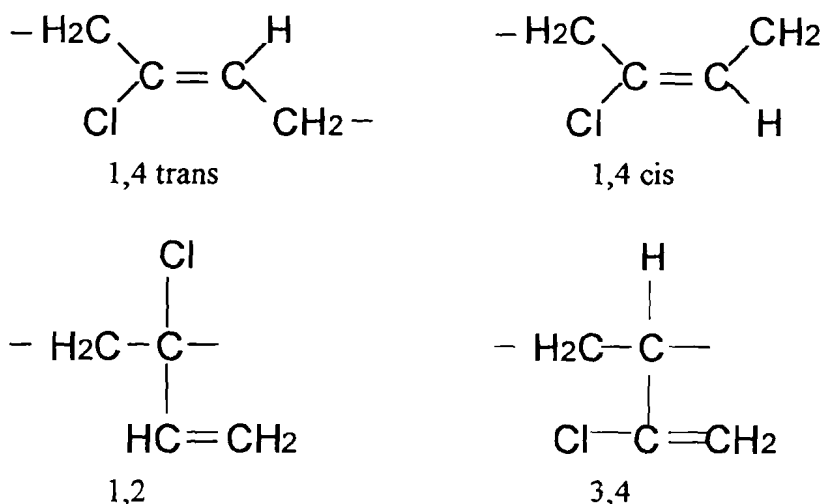
For both dry and latex CR, there are four key polymer properties which affect adhesive properties. Their understanding helps the formulator to choose the right product for a specific end use. They are listed in the following table.

desired property	process variable
crystallinity	polymerization temperature
gel content/ MW	conversion, chain transfer
polarity/ adhesion	comonomer
reactive sites	comonomer

Crystallinity is one of the most important properties of the polymer. It is the tendency of the molecules or segments thereof to order themselves in a three-dimensional array. It is a reversible physical phenomenon that may be destroyed by heating above ca 40 deg C. The degree of crystallinity determines the modulus of the glueline and the cohesive strength, the rate of crystallization the development of cohesion and the open time. Both go normally in the same sense.

Crystallinity can be controlled because of the nature of the monomer which can enter the chain backbone in four possible configurations:

Fig. 1: configurations in Polychloroprene



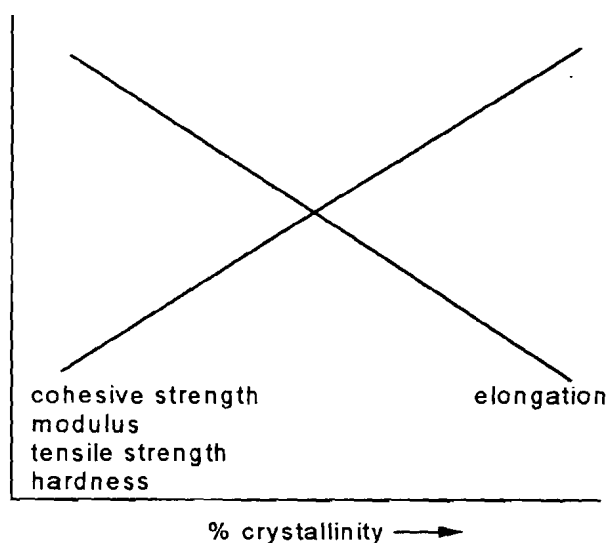
The most favoured is the 1,4 trans configuration. It is sufficiently regular and the polymer becomes crystalline. All other configurations act as impurities and reduce the chain regularity and thus crystallinity.

The crystallinity is essentially controlled by the polymerization temperature. Low polymerization temperature leads to high 1,4 trans structure. Higher temperatures promote formation of the other configurations. Crystallinity ranges between 0 and 25% crystalline phase for commercial grades of CR. The crystalline melting point is between 45 and 50 deg C. The glass transition of CR is -45 deg C.

Another method to reduce crystallinity is use of a comonomer, especially 2,3-dichloro-1,3-butadiene. Comonomers break up the chain regularity and disturb crystallite development. Higher comonomer levels will raise the Tg slightly, but this does not affect the adhesive properties significantly.

Fig. 2. polymer properties vs. crystallinity

Effect of crystallinity on polymer properties



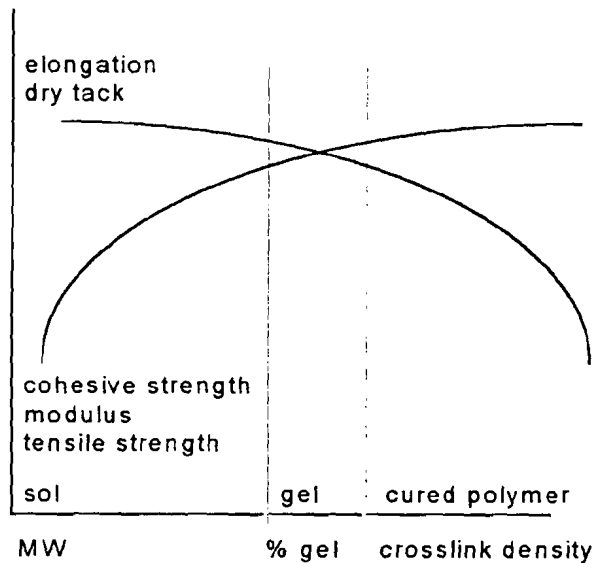
The second important property is the MW for soluble polymers or the fraction of crosslinked polymer, the 'gel'. Solvent adhesive grades must be gel free, otherwise they become insoluble. The molecular weight determines the solution viscosity. Latices can contain gel without any apparent changes in rheology. The amount of gel is controlled by the degree of conversion. With the ratio polymer/ monomer, the likelihood that free radicals encounter polymer chains increases, resulting in chain branching and crosslinking.

Higher conversion also results in higher latex solids.

One important characteristic of sol polymers is the ability to be heat reactivated- this is one way to enable quick bonding but on the other side the hot bond strength is limited by the crystalline melting point of the polymer.

Fig 3: polymer properties vs. gel level

Effect of sol, gel and cure on polymer properties



Increasing crystallinity and gel give an increase in cohesive strength, modulus and heat resistance. Tack, open time and elongation are reduced. Fig.3 shows the zone where the most suitable latices for water based adhesives are located.

The last possibility to modify the polymer is by copolymerization with functional monomers, i.e. methacrylic acid. The reduction of crystallinity is only a side effect—more importantly it introduces cure sites which can be used to crosslink the polymer and thus enhance cohesion and hot bond strength. Acid groups also enhance the adhesion to certain substrates such as metals.

**formulating?: think water based!**

The primary aim of the adhesives formulator when moving from solvent to waterbased adhesives is to match the properties of solvent adhesives as completely as possible. However, working with the same polymer does not always mean identical properties. It is important to understand and compare the mechanisms of film formation to identify the right way formulating.

In the solvent adhesive, we have a completely homogenous solution of polymer and resin. As the solvent evaporates, the chains approach each other and will eventually crystallize once all the solvent has evaporated. There is a clear transition from fully amorphous to crystalline and there are several ways to control the drying time, the open time and the development of cohesion by choice of polymer, resin and solvents.

Another positive characteristic of solvent systems is their low surface tension: they wet low energy surfaces very readily and tolerate also some surface contamination by e.g. greases. In addition, they swell rubber or plastic and facilitate interdiffusion between substrate and adhesive.

In water based, we start with a dispersion, a heterogeneous system. Polymer and resin are discrete particles, held in suspension by surfactants. As the water evaporates, the particles approach each other, deform and eventually weld together through surface forces. At this moment, there is also a phase inversion: The water which was the dispersed phase so far becomes encapsulated in voids in the film, resulting in a dramatic reduction of the drying rate. The dispersed polymer is supposedly amorphous and crystallizes as the film dries, but the autoadhesion is far inferior to that found with solvent adhesives.

The principal reasons are:

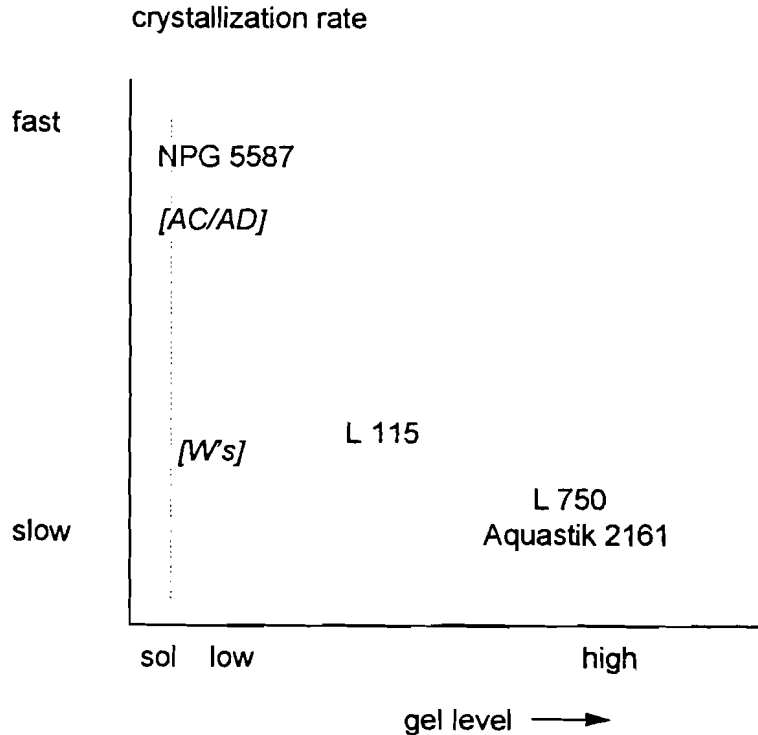
- absence of residual solvent: no softening/ tackfying effect.
- presence of residual soaps and surfactants. These are in most cases incompatible with the polymer film and migrate to the surface where they reduce the tack.
- tackyfier not dissolved in polymer, no plasticizing effect.
- gel content in most latices

At this point we could jump to the conclusion that most things except toxicity and fire hazard are just right with solvent adhesives and about everything except the non flammability is wrong with water based. This does not take into account the flexibility we have on the polymer side and the options on formulating properly.

### **Choice of polymer:**

The best way to visualize the polymers is in a two dimensional graph, with crystallization speed at the y-axis and gel level at the x axis. Typical products are on a diagonal, going from top left to bottom right. For reference, the solvent grades would all be located at or close to the Y axis because they are (must be) gel free.

Fig. 4: Polychloroprene latices for adhesives



For latex adhesives, products tend to be located along a diagonal, starting with low gel, fast crystallizing products at top left and moving to high gel, slow crystallizing grades at the bottom right. The latter are preferred because we cannot rely on residual solvent in the film to give a low modulus and sufficient autoadhesion, but have to build this into the polymer- therefore the need for slower crystallization on one side and some gel to provide sufficient nerve on the other.

Fig. 4 shows four typical candidates. NPG 5587 is a fast crystallizing gel free latex. Although this polymer is very similar to Neoprene AD, its behaviour in water based adhesives is very different from solvent based adhesives because of the different carrier. It has very low tack and the main use would be in wet bond adhesives. The other extreme is Latex 750, a slow crystallizing high gel latex which combines some contactability with good hot bond strength. An upgrade of this product is Aquastik 2161 whose hot bond strength is further improved compared to Latex 750.

Somewhere around the center is Latex 115- a carboxylated nonionic latex with low to medium gel and slow crystallization. This product has been optimized to give a suitable balance between contactability and nerve.

Compared to solvent grades, the obvious choice for water based contact adhesives is a low modulus polymer, because the softer film also gives more contactability. The lack of crystallinity can then be compensated by a suitable gel level to provide sufficient 'nerve' = cohesion. This is clearly different from solvent adhesives where the modulus changes as the adhesive crystallizes. Formulating is preferably done in the window shown in picture. Choice of the right polymer for a given end use is



one thing, but formulating is at least as important. Going back to Fig.3, the polymer choice gives the starting point, the art of the formulator allows to upgrade certain characteristics.

We will not cover the whole subject of formulating here- but just look at two examples and highlight the essentials.

### **1. Contact adhesives :**

The principal requirements for contact adhesives are:

- reliable bonding under low pressure -> contactability
- green strength
- short drying time
- long open time
- hot bond strength

These are listed in the order of importance. It appears difficult to compromise on the 'grab'- this is the key property. Therefore the polymer has to be of low modulus type - that means slowly crystallizing. For sufficient nerve (green strength) it has to contain a certain amount of gel. Both parameters also take care of open time and hot bond strength. The drying time is the most difficult to control- it depends to some extent on the overall solids content but mainly on the emulsifier system, on the presence of thickeners and to a very large extent on the water vapor barrier properties of the polymer film which determine the drying rate after coalescence.

The two preferred products are Latex 115 or Aquastik 2161. Both are slow or non crystallizing.

The carboxylated Latex 115 reacts with Zinc oxide and the resulting ionic crosslinks give a rapid development of cohesive strength. Aquastik 2161 is higher in gel and slow crystallizing- here the gel provides the green strength and hot bond strength, the slow crystallization gives a low modulus film with good tack. The second important component in contact adhesive formulations is the tackifier resin. Typical products for contact adhesives are rosin esters and terpene phenolic resins, often used in combination. The rosin esters provide excellent tack and contactability, whereas the terpene phenolics contribute specific adhesion to e.g. metals.

There is a broad range of commercial dispersions available- most critical is the compatibility between resin dispersion and polymer latex to ensure processing and storage stability. Compatibility for water based adhesives does not only mean compatibility between the resin and the polymer which is important for the cohesion. It also includes compatibility between the emulsifier systems to avoid destabilization of the latex or erratic changes in viscosity.

A more recent development is a liquid rosin ester which contains surfactants and can be easily direct dispersed in nonionic latex. It provides very good tack but needs to be combined with a high melting resin to obtain sufficient bond strength. The approach is very interesting because it allows to increase the solids level of the overall formulation.

Similar effects can be obtained by combining nonionic Polychloroprene latex with other dispersions, such as vinyl acrylic, PVDC or Polyurethanes. All these systems function similarly to resins. They enhance specific adhesion, unfortunately often at the expense of contactability. It is important in all these blends to use Polychloroprene as the major component, in excess of 55%, to maintain a sufficient level of contactability. Films formed from latex blends are two phase systems and it is essential to have a continuous PCP phase to take full advantage of its properties.

## **2. Wet bond/ quick break adhesives:**

NPG 5587 is a fast crystallizing/ sol latex and very similar to the AD types. The dry film from latex does not show any significant tack but due to the fast crystallization already wet films have sufficient cohesion to bond porous substrates, e.g. upholstery foam or textile. Typically formulations are adjusted to relatively low shear stability so that they can just be spray applied but coagulate very quickly through the initial moisture loss to the substrate and the joining pressure. This 'quick break' effect replaces the autoadhesion of the dry solvent adhesive film. It can be used only on porous substrates where the moisture can dissipate and evaporate after assembly. The high modulus film normally has enough strength to keep parts together even under stress.

In this particular application, Polychloroprene is often used blended with an Acrylate dispersion. The latter provides some initial tack and has also a destabilizing effect which accelerates coagulation.

These quick break adhesives meet an urgent need of the industry to substitute non flammable adhesives based on chlorinated solvents. Alternative systems can be based on slower crystallizing, more stable latices which are co-sprayed with a coagulant, such as weak acids or salt solutions, to obtain fast coagulation once the latex hits the foam surface.

Another side option with adhesives based on NPG 5587 is the possibility to heat activate: The adhesive can be applied to parts and after complete drying reactivated at any moment. The advantage of this process is that we get a complete decrystallization similar to that obtained with solvent adhesives, therefore an aggressive grab, and after assembly a very fast development of the cohesive strength.

These two examples highlight what can be done today with existing grades- there are opportunities in a number of other important end uses such as footwear

adhesives where properties like plasticizer resistance and colour stability are important and these are being pursued.

Without going further into details, it becomes obvious that the transition from solvent to water based needs close support. Rather than supplying just the adhesive, the adhesives manufacturer should offer a whole package which includes also the application technology- i.e. advice on machinery, processing etc. to ensure the transition goes smoothly. The same applies to raw material suppliers.

With the increased complexity of the water based systems and the need to formulate more specifically for a given application, it is in fact essential to identify the needs of the end user properly prior to selecting a polymer and then formulating the adhesive around it. Looking at the currently available dispersions on one side and the options on the other, there is still considerable potential to provide improved products which satisfy the needs of the industry.

Cost is often mentioned as an disadvantage of water based systems. To analyze costs properly, we have to go down again the whole chain. On a volume:volume basis water based adhesives must be more expensive because they contain more solids. On the other hand manufacture which is a mix & stir operation will be faster and cheaper. The cost of the glueline should be roughly equal if we take into account the smaller amount of liquid adhesive needed for the same or higher coverage. Cost for ventilation/ solvent reclaim are not considered here but will definitely work out in favour of water based systems.

## **Summary**

In spite of its mature age, Polychloroprene is a very attractive product for the formulation of water based adhesives and still has considerable development potential. Its chemistry is very versatile and allows to design products which help to carry the versatility and performance of traditional solvent based systems over to water based adhesives. Formulating and handling of the finished adhesive are going to be different and will require some changes in application techniques but these will be overcome if raw material producers, adhesive manufacturers and end users work together closely.