

## **Vacuum coating - some considerations on adhesion or lack of adhesion**

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### **Introduction**

We need good adhesion between flexible substrates and coatings because we are increasingly using the coated material in applications where there is stretching and bending. If the coatings are not well adhered the coatings will crack, buckle or delaminate and lose their function. We are familiar with the move to flexible circuits, displays and lighting as well as the lower specification flexible packaging but there are also the newer applications such as flexible functional fabrics that range from fashion clothing with novelty additions such as lights including changing colours and patterns. There is also the more useful functional clothing where the fabrics include sensors to monitor the wearer for the likes of pulse rate, temperature, perspiration level and breathing rate. To obtain good body function measurements the garments need to be close fitting and for the person to move easily the fabric needs to be able to stretch considerably, more than would be expected of electronics such as displays. Hence as the applications get more difficult to achieve the attention to adhesion is increasing.

Often it is assumed that the film as supplied is a constant when, most of the time, it should be considered as a variable. It is also often assumed that buying equivalent film from different suppliers does not matter but this is not necessarily true and often it too is another potential variable. This paper considers some of the factors that ought to be considered when trying to obtain good adhesion of vacuum deposited coatings.

### **Adhesion**

Measuring adhesion is not easy particularly if you want to obtain a reliable and reproducible value. There are easy tests such as the tape test that give a quick pass or fail answer but tell you little about how good the adhesion might be. Other tests such as the fragmentation test are much more time consuming but will deliver a value for the adhesion. One observation that can be made when using the fragmentation test is the onset of cracking. This is the point where the first crack across the tensile test sample is observed. This can be used as a short cut to ranking adhesion when changing substrate or processing.

A good site of information is <http://www.stevenabbott.co.uk/PracticalAdhesion> where the various types of adhesion are described. A more detailed work on adhesion (1) from the same author is also available. The basic low adhesion can be regarded as being related to proximity through the likes of Van der Waals forces. To obtain high adhesion, anywhere up to 1000x increase over proximity adhesion, requires something more than a coating being in

intimate contact with the substrate. There are two aspects to getting high adhesion, entanglement and chemical bonding. The chemical bonding is just as it sounds there needs to be a direct bond between the coating and the substrate. This usually requires the polymer to be treated to break open some chains and provide end chains that are available for the coating to bond to. The breaking of bonds needs to be done with some care as too much breaking of chains can lead to a weakening of the surface as the short chains are no longer well bound into the bulk polymer and have no entanglement. Entanglement is where the polymer chain has at least 3 points of contact in the bulk polymer. To get good adhesion requires the energy being used to pull the layers apart being absorbed either directly in the energy to break the chemical bond or via some other mechanism. Calculations have been done that show the highest adhesion requires more than just direct chemical bonding. The analogy has been given of trying to pull out one piece of string out of a tangled bundle. When pulling one piece of string it will extend and then the entanglement will cause other strings to be lifted with it, which requires energy. Eventually the energy required to lift the tangled string will be greater than that required to break the string and the string will then break. The other analogy is sticking something to some chewing gum where as the item is lifted the chewing gum extends elastically so dissipating energy. If the chewing gum is frozen the adhesion drops considerably as the chewing gum changes from being elastic to becoming rigid and so loses the ability to absorb energy.

Earlier work has shown that modifying the polymer surface to minimise the inelastic crystalline proportion and increasing the more elastic amorphous proportion increases adhesion (3).

### **Polymer substrates**

It is nice to think of substrates as being a constant but they are far from this. If the polymerisation is anything less than 100% there will be some short chain low molecular weight oligomer still present in the substrate bulk. This low molecular weight material can migrate from the bulk to the substrate surface. The rate of migration will depend on the material, the molecular weight as well as the temperature. The higher the temperature the faster the migration rate and the longer the time the more will have accumulated onto the film surface. So the surface energy will change from a high at the point the web was produced and will gradually decline until the surface is completely covered with low molecular weight material. The measurement of surface energy can be considered as a measure of contamination. If the surface is pre-treated such as by a corona plasma treatment the surface energy will increase as some of the low molecular weight material is either removed or modified. Following any pre-treatment the surface energy will resume its decline as additional low molecular weight material migrates to the surface. Before any vacuum coating process it would be useful to have knowledge of the age and temperature history of the substrate. Unless the age and temperature history are identical the amount of surface contamination is likely to be different which would suggest that any plasma treatment should be adjusted if the optimum treatment is required to achieve the maximum coating adhesion.

Too little treatment would leave some low molecular weight material on the surface which would reduce the possible adhesion. Too much treatment would cause surface damage of the polymer with too much chain scission creating polymer fragments which would also lead to a loss of adhesion.

## **Web cleaning**

Roller cleaning has been done using tacky rolls and also using fabric rollers that narrow and sequentially moved across rollers or drums. The latter has been used specifically for cleaning oligomer off casting drums. This does indicate that gross contamination of surfaces can be removed and that oligomer is poorly adhered however the fabric cleaner used works in a similar way that an operator would use a polishing cloth. The cloth has a fixed surface and so the oligomer is smeared across the rotating drum surface as well as being transferred to the fabric. The fabric needs to be moved and refreshed as the oligomer accumulates on the fabric. I would be concerned about using this cleaning technique on a polymer web as any particulate trapped along with the oligomer would cause scratches on the soft polymer. This does suggest that the adhesion or cohesion of the oligomer is poor and so the tacky roll should be suitable for being able to lift off oligomer and transfer it to a high adhesive roll. The question is then how well can a tacky roll system remove oligomer from a polymer surface. I have not found any answer to this question and my suspicion is that it could lift off the oligomer a monolayer at a time and so require multiple tacky rolls to fully remove oligomer from the surface. If this is the case it would make the process impractical for completely removing oligomer. Washing can be used to remove low molecular weight material however the problem with this is that it is hard to clean the surface perfectly. Once the low molecular weight material is taken into the wash liquid the liquid needs to be removed completely from the film surface. In addition some of the liquid may be adsorbed into the polymer and this will be released in the vacuum system. Washing usually requires several washes starting with the cleaning solution which needs to be followed by further baths to clean off the cleaning solution. As it is difficult to remove the all residues the film still needs to be followed by a plasma clean. Thus washing is often regarded as expensive with little benefit over just using plasma cleaning.

## **Conclusions.**

Obtaining good adhesion sounds simple enough. The polymer needs to be first cleaned of all poorly adhered molecular contaminants. Then the surface needs to be conditioned to enable chemical bonding to bulk polymer that has entanglement and with some elastic properties.

As a minimum it is important that the surface has a plasma treatment to match the amount of surface contamination which has accumulated and will relate to the elapsed time, the storage temperature and oligomer type or molecular weight. It is not too surprising that where a constant plasma power density is used for all film that the adhesion may be variable.

## References.

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