Etching & texturing polymer films - different options for patterned deposition or encouraging nucleation.

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Abstract.

A number of the nanotechnologies or psuedonanotechnologies depend upon controlled nucleation and growth of coatings. Often the coatings remain as a discontinuous structure or islands. It would therefore be useful to control the nucleation process to encourage a regular deposition pattern & then to produce islands of a regular uniform size.

The basic idea is that nucleation can be influenced by the surface texture. It has been shown in nucleation studies that nucleation will take place preferentially at steps on the surface as nucleating against the step offers an extra reduction in surface energy. Thus producing steps or equivalent defects in the surface can help encourage nucleation to take place at these sites.

It has often been commented that roll-to-roll coating is the expected route to market if this type of product is to be produced economically. However there has been little done to look at the options to develop some of these processes to make then suitable for roll coating.

In this paper I will try to give some details textured polymer films, by what methods they have been textured and if this might be feasible for inclusion in a roll coating process.

Polymer surface texturing options.

There are a whole range of options for texturing polymer surfaces and huge variety of methods of producing these surfaces.

The different methods can be separated into two broad classifications, random texturing & regular or patterned texturing. The random techniques would include the processes such as liquid, plasma or laser etching and generation of hairy surfaces. The production of regular structures would include techniques such as embossing, laser writing or printing.

Obviously the type of product or coating required will determine the surface required & technique to produce it.

If the surface is going to be coated with a catalyst then it is likely that a method of producing a high surface area will be required. One option would be to produce a ‘hairy’ surface by a technique such as tack melt spinning (1). Other simpler options could be used with the higher surface area produced by chemical etching, abrasion or even a high density of fillers into the polymer surface. These would have a higher surface area than the basic polymer film but lower than the hairy surface texturing.

If the coating is aimed at optimising the plasmon performance or at nucleating the crystal structure for creating photonic type material then a smooth surface with a precision pattern etched or embossed into the surface might be used to advantage.

Random surface texturing.

Tack melt hairy surfaces

This process has the simple concept of melting the top surface of the polymer web, using a roll to touch the molten tacky surface & pull up hairs from the surface with a blade cutting the hairs to length. This type of product has been made for use in packaging applications where a velvet-like surface is required.

Figure 1 on the right shows a schematic of the basic method for producing a web with a hairy surface.

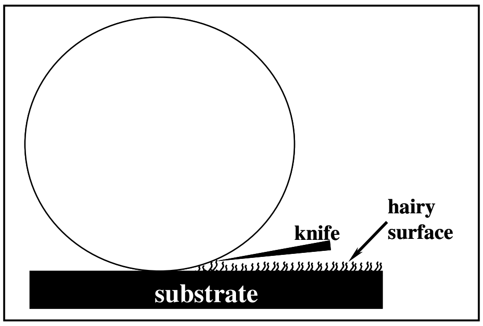


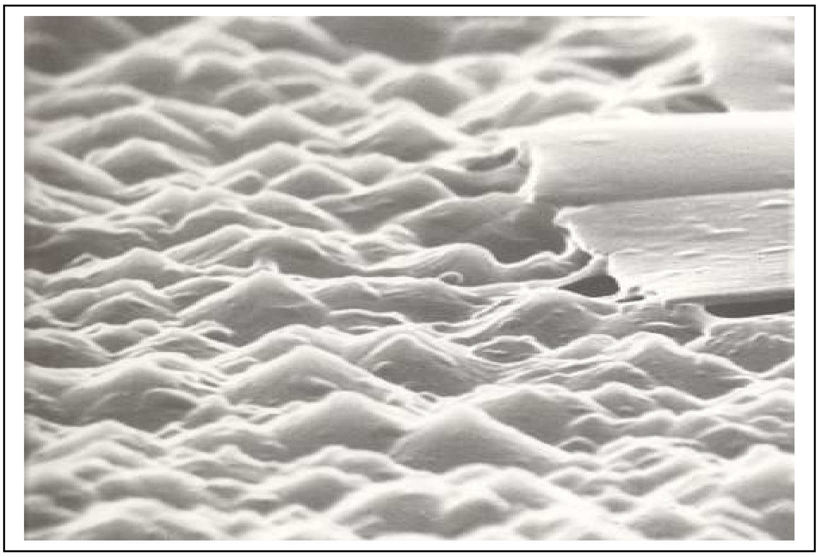
Figure 1. Tack melt process

Surface etching

There are two main methods of etching the surface. The oldest method is to use the appropriate liquid to etch away the top surface. For instance polyester terephthalate (PET) can be etched using orthochlorophenol (OCP) at an elevated temperature. The disadvantage of this technique is the use of chemical baths which can be expensive & with large environmental costs.

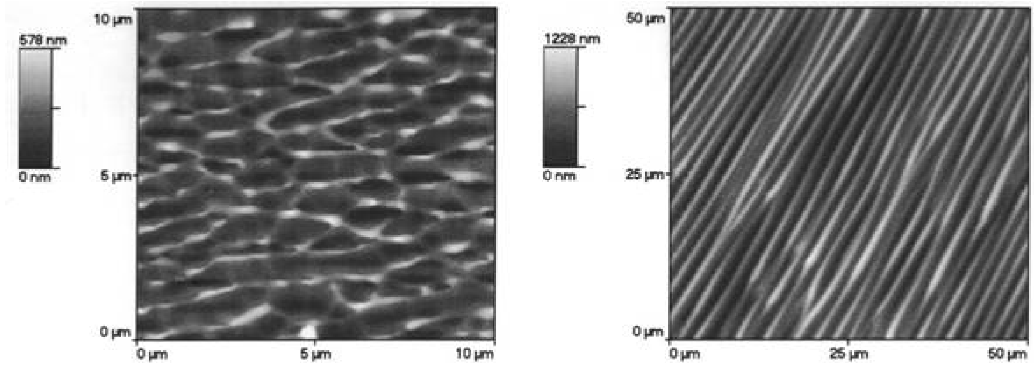
Figure 2.

'O' grade Melinex etched using boiling hot orthochlorophenol



An example of an etched PET is shown above, the flat surface is where an oxide coating protects the surface. The surface shown is for an unfilled PET. A different structure could be produced if the PET contained fillers that could become exposed by the etching process.

An alternative method of etching away the polymer surface is to use laser ablation. (2,3) Examples of this are shown below.

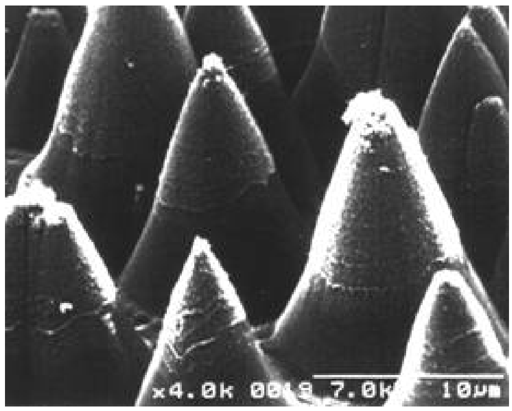


Atomic force microscope picture of the surface structure developed on the ablated PET film at 0 and 85 degrees. Dyer et al. Hull Univ.

Figure 3.

One of the useful things that the laser can do is change the shape of the features produced by changing the rate, duration & angle of etch by the laser beam. As can be seen from figure 3 changing the angle squashes the shape of the etch depressions & the irregular circular shapes change to the shape of stretched elliptical pits.

If the etching is continued at high rates the structure changes again this time to produce cones. Again if the angle is changed the cones can become angled & extended in one orientation. The figure (right) is for the laser etch being normal to the surface and producing a regular array of cones.



Scanning electron microscope picture of the developed conical structure on excimer laser irradiated polyimide at 74.4 mJ/cm2 fluence.

Figure 4.

What can be seen from the micrographs is that the surface is not free of debris following the ablation & hence might need some cleaning process

Additives can affect the interaction of the laser with the polymer & so switching substrate manufacturers can result in different structures for the same conditions.

Regular or patterned texturing.

These techniques are aimed at producing a texture such that a precise array of nucleation sites & then islands are formed. There are three techniques commonly used are laser writing, printing & embossing. All of these tend to have dimensions of around a few hundred nanometers to a few tens of microns. This dimension tends to be much larger than the aimed for island dimensions that tend to be of the order of 2 to 50nm.

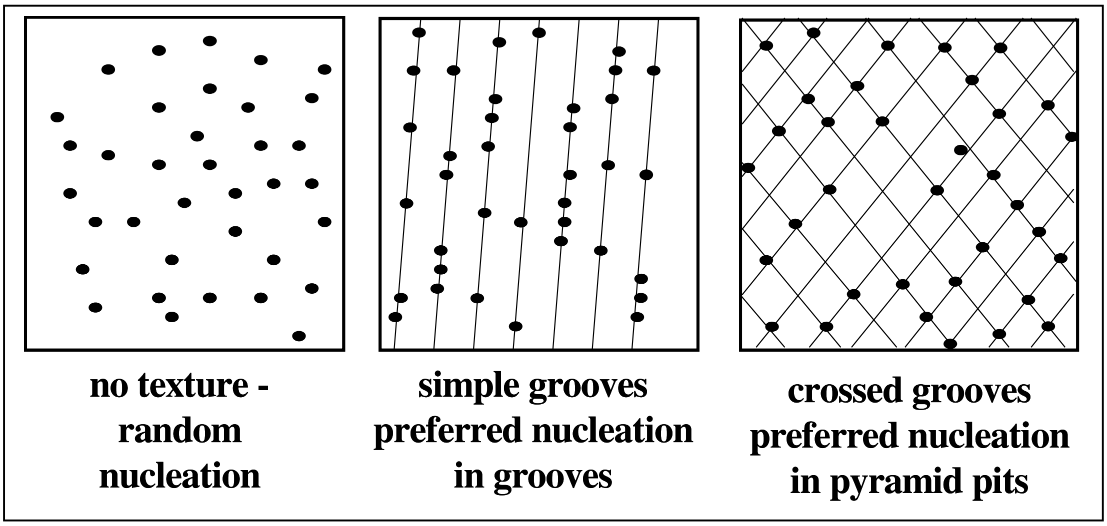


Figure 5.

Figure 5 above shows a schematic of what is aimed for in producing a regular structure to help the nucleation to be initiated. The middle schematic shows the effect of simple grooves where the nucleation sites may be in the grooves and so separated evenly between each groove but randomly within each groove. The right hand schematic shows the crossed grooves where the encouragement to nucleation is at the intersections of the grooves and hence the nucleation sites are more evenly spaced in two dimensions.

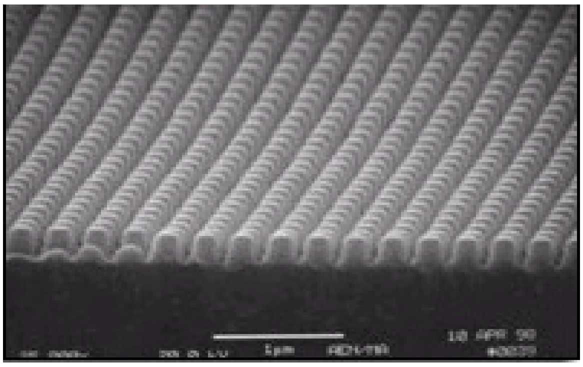
Embossing.

There are three key factors that need consideration relating to the embossing. The first is the origination. The smaller the pitch of the pattern the shorter the wavelength needed to make the origination. It is possible to produce very fine pitch shims but it may require e-beam writing which takes a very long time for large area shims or needs exceptional tiling techniques to build up a large size shim.

The next consideration is that as the structures become finer the surface they emboss into needs to be flatter & smoother with fewer surface defects. This requires the polymer web surface to be cleaned and a smoothing layer to be coated over the remaining debris.

The final consideration relates to the embossing (4). As far as I am aware this has not been done in-line in vacuum and so this needs to be developed as a process. Often when starting up an embossing line the operator has to make changes to the process and may even need to clean the shim & apply a release coating to help the shim release cleanly from the embossable polymer. To do this the operator needs a very clear view of the shim and embossed web. Use of release sprays would not be available within a vacuum system & getting a clean embossing may prove to be hard to achieve. Hence some experience & development is going to be required.

An example of a standard motheye Structure (5) is shown in Figure 6 the micrograph on the right. The pitch of this sinusoidal structure is 300nm which makes the structure invisible to the naked eye. This would make the embossed surface anti-reflecting by grading the refractive index from air to the refractive index of the polymer.



300nm pitch replicated holographic motheye Structure as produced by Holographix

Figure 6.

By embossing only part of the full depth of the structure the surface will have indentations that will act as advantageous nucleation sites but because of only embossing part of the structure the shim will be less inclined to become clogged. However this does required that there is much more precise control of the embossing pressure and/or shim position than in conventional embossing. .

Printing

In-vacuum pattern printing is now available from a number of suppliers (6,7). The resolution is gradually being improved & features of 50 microns can be reproducibly printed. Work is continuing to develop the roll technology to enable finer lines to be printed. The line width depends on the engraved roll hardness, the quality & type of laser engraving used as well as the control of the amount of oil applied to the roll.

All of these features are much larger than those typically produced by embossing but the technology has the advantage that it is proven to work in vacuum.

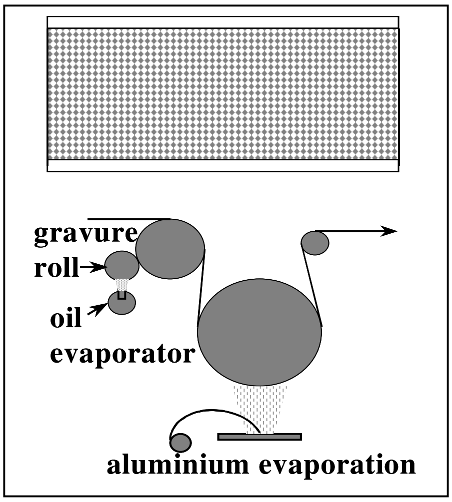


Figure 7.

Ink jet printing is another printing technology that could be used. Ink jet printing has been done in vacuum and may have some advantages. Previously the width & speed of large roll-to-roll vacuum coating systems tended to prevent ink jet technology from being used. However with the envisioned smaller production machines & likelihood of using some low deposition rates & hence winding speeds this print technology looks more promising.

One of the advantages would be that the pattern could be changed mid-roll without the need to break vacuum. Also as single nozzle could produce a single line there is no reason why the fine line capability should not be reduced to better than 10 microns.

Cleaning

The liquid surface etching can almost be regarded as a self-cleaning process as the liquid retains the polymer waste material. The laser etching may produce powdery debris that needs to be removed. This may be done outside the vacuum system by processes such as ultrasonic pulsed air jet & vacuum cleaner with electrostatic neutralisation or by tack roll cleaning (8).

The printing process would benefit from a clean web in that there would be fewer printing defects. The process that would most benefit is however the embossing process where to get the finest embossed structure the web needs to be very clean & smooth before the embossing. This could be carried out outside the vacuum system so long as all the processes are done within either a cleanroom or under clean hoods within a clean area. Inside each hood is effectively a high specification clean room but by being localised it reduces the overall cost.

What would be ideal would be to do several of the processes within the vacuum system immediately before the deposition so that the surface is as clean as possible.

This sounds good in theory but some of the processes are, as yet, unproven in vacuum. There have been trials using tack rolls inside the vacuum system but there have been problems with the tack materials. They tend to lose some of their tack under vacuum & so work less effectively. Also as the tack roll becomes clogged with debris there is no easy mechanism for refreshing the roll by peeling off the top clogged layer & revealing the next tacky accumulation layer. Thus the effectiveness of the roll falls off down the length of the rolls.

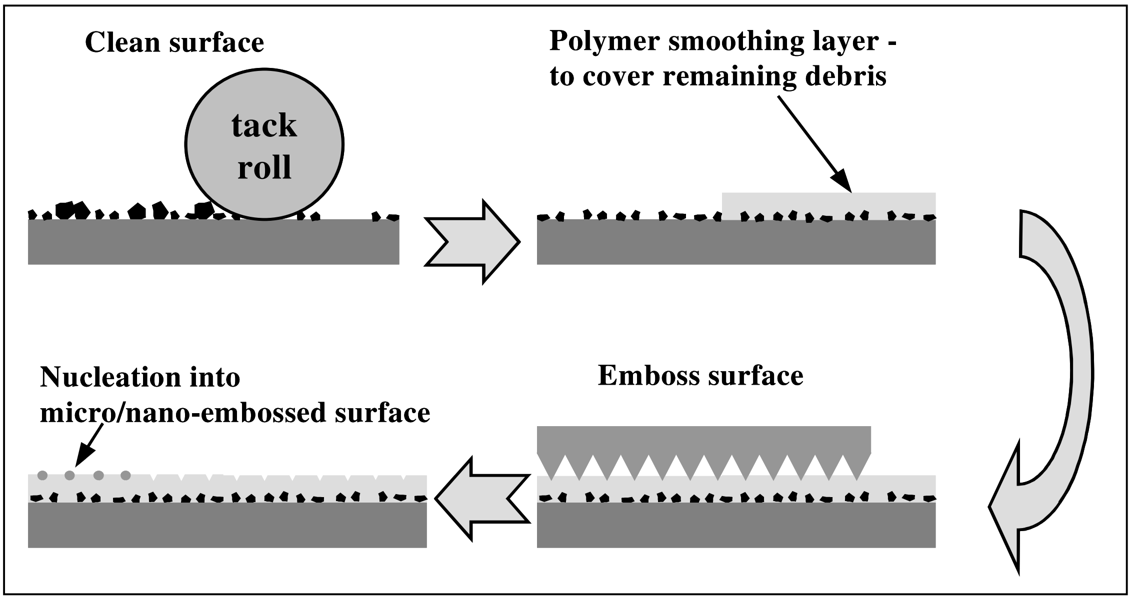


Figure 8. A schematic of the different steps that need to be developed as an integrated process within the vacuum system.

Discussion.

As mentioned earlier embossing is not usually carried out under vacuum & this too needs development to make the process robust enough to be considered for production. Typically where an embossing passes through a vacuum roll-to-roll coater the embossing has been done outside the vacuum.

The one process that has been achieved in vacuum is the deposition & cure of the polymer layer used to cover the debris & smooth the surface (9). This could be used to deposit very thick polymer layers to cover all of the debris irrespective of size. Although it would be preferred to reduce the size of the remaining debris as much as possible & only have to deposit a relatively thin polymer-smoothing layer.

Like all surfaces even this newly deposited polymer may need the surface to be chemically modified to improve the wetability and control the nucleation process. Thus not shown in the schematic there will be a plasma processing step too.

As many of the products envisioned are very small items the production capacity of what used to be thought of as a research & development machine could be expected to be sufficient for full-scale production. Thus the development work to integrate these processes would not have to be repeated on further scale-ups.

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