

ASYMMETRIC MEMBRANE STRUCTURES AS A RESULT OF PHASE SEPARATION
PHENOMENA

L. BROENS, F.W. ALTENA, C.A. SMOLDERS

Twente University of Technology, Department of Chemical Engineering.
ENSCHEDE, The Netherlands.

and D.M. KOENHEN

Wafilin Membrane Filtration Systems, Hardenberg, The Netherlands.

ABSTRACT

In this report we give a description of the membrane formation mechanism based on theoretical and experimental knowledge of phase separation phenomena in concentrated polymer solutions. We demonstrate that different types of phase separation are responsible for the build-up of the dense skin layer and the porous supporting layer in asymmetric membranes of several materials: cellulose acetate, polysulfone polyacrylonitrile and polydimethylphenylene-oxide. The formation of the porous sublayer will be explained in terms of liquid-liquid phase separation, coalescence and gelation. Special attention will be paid to the formation mechanism of the finger-like cavities in the sublayer. A possible explanation will be given on thermodynamic and kinetic grounds, for the formation of nodular structures in the skin of the membranes.

I INTRODUCTION

The majority of the commercially available membranes are produced by the so-called phase inversion process, starting from a polymer solution which is precipitated in a non-solvent coagulation bath. The resultant membranes prepared in this way have an asymmetric structure, i.e. a very thin more or less dense skin is supported by a porous sublayer of the same material. The technique of producing membranes by the phase inversion method has reached a high degree of reproducibility. This development has been sustained by many systematic studies of the effect of relevant parameters and by the efforts to elucidate the mechanism of membrane formation¹⁻¹²⁾

The phase inversion process is of a highly complex character, in

which phase equilibria, the kinetics of phase separation and changes in morphological structures in non-dilute systems play a role. Phase separation phenomena in dilute polymer solutions have been studied intensively. This is not the case for concentrated polymer solutions, due to experimental difficulties and the complexity of a quantitative theory. We feel that it would be of great value for the improvement of membrane preparation processes if our knowledge of phase separation phenomena in polymer solutions could be extended to the medium and high concentration region.

In this paper we present a description of different types of phase separation phenomena in concentrated polymer solutions. Cloud point curves and calorimetric (DSC) measurements will give indications which phenomena can occur in different compositional regimes. The question will be discussed which factors during the formation of the skin determine the membrane type: ultrafiltration or hyperfiltration membrane. Cavity formation in the porous sub-layer will also get special attention.

II THEORETICAL CONSIDERATIONS ON PHASE SEPARATION IN CONCENTRATED POLYMER SOLUTIONS

The following types of phase separation phenomena in polymer solutions can be distinguished:

- liquid-liquid phase separation
- crystallization of the polymer
- gelation

1. Liquid-Liquid (L-L) phase separation

When a homogenous solution becomes thermodynamically unstable, e.g. by the introduction of a non-solvent, the original solution can decrease its free enthalpy of mixing by splitting up into two liquid phases of different composition. In figure 1 a schematic drawing shows such a free enthalpy surface and following the line A B C D E one sees that all compositions indicated by points between B' and D' of the phase diagram will split up in two phases of composition B' and D'. This process is called liquid-liquid phase separation. There are two kinetic ways for L-L separation to occur: either by nucleation and growth of the second phase or by spinodal decomposition. Entering the miscibility gap e.g. at the side of B' (this is a concentrated polymer solution with a certain, low amount of non-solvent) a nucleus of composition D' (this is a drop of high non-solvent content with almost no polymer

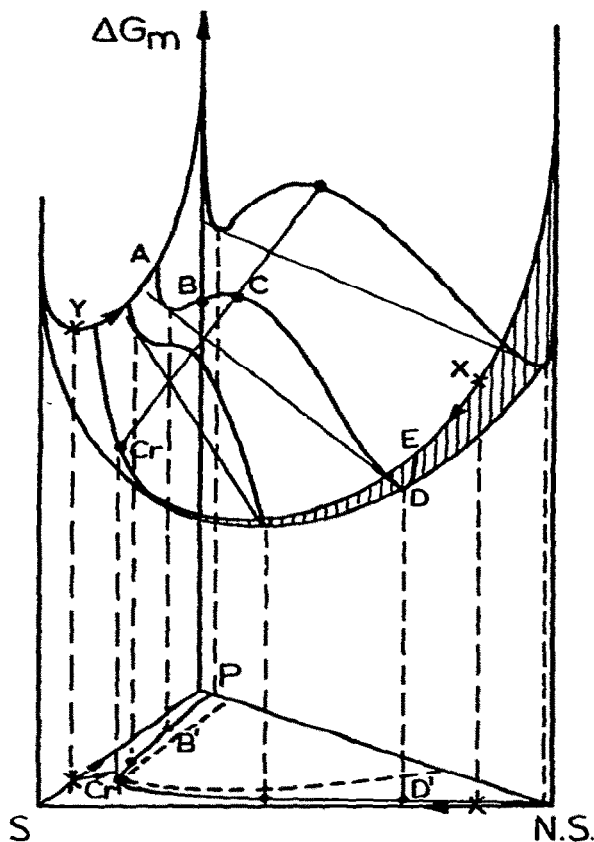


Fig. 1 ΔG_m surface for the system polymer (P), solvent (S), non-solvent (NS).

in it) will be formed in the polymer solution. This nucleus together with many other nuclei, will grow to droplets until they touch each other and coalesce or until their growth stops because of gelation of the surrounding polymer solution. The second kinetic way to L-L phase separation would occur if one could so quickly enter the miscibility gap at point B' that one would pass the dotted line (the spinodal) before nucleation could take place. For those compositions the solution is unstable with respect to infinitesimal small concentration fluctuations. The solution then separates spontaneously^{13,14)} (by diffusion of molecules) into interconnected regions of high and low polymer concentration ending up in intertwined networks of phases with composition B' and D'.

Of course here also much would depend on rheological behaviour to find this pattern conserved in later stages of the separation process. As a matter of fact spinodal decomposition is a highly improbable phenomenon in polymer solutions, since nucleation and growth kinetics are too fast for the homogeneous solution to reach the required composition region.

Of course it is easy to draw the connection now between L-L phase separation and the genesis of the porous sublayer in membrane formation¹¹⁾ (see also section IV). The most interesting question here is, which of the polymer phases will be nucleated when starting with a normal membrane casting solution. In principle two possibilities exist, depending on the composition of the initial polymer solution with respect to the so-called critical point, point C'_I in figure 1. For concentrations higher in polymer concentration than C'_I (hence lying on the branch C'_I B') the nuclei will

consist of the dilute phase. The reverse is true for initial polymer concentrations below C'_R (branch $C'_R D'$). Now the critical point in polymer solutions is generally located at rather low polymer concentrations (< 10 weight percent in polymer). Since membrane forming solutions contain in general more than 10 weight percent of the polymer one should expect L-L phase separation with nucleation and growth of the dilute phase to be the rule.

2. Crystallization and gelation¹⁵⁾

When the thermodynamic quality of a polymer solution is decreasing which may occur by loss of solvent, by lowering of the temperature or by the introduction of a non-solvent, most polymers are able to form ordered agglomerates. In very dilute solutions the polymer molecules can form single crystals of lamellar type, being only a few hundred Angströms thick and often many microns in the lateral direction. From solutions of medium concentration more complex morphologies occur i.e. dendrytes or spherulites. These latter structures may contain, except for the ordered regions, appreciable amounts of amorphous polymeric material.

The formation of ordered structures is dependent not only on the thermodynamic quality of the solution but also on the ability of the macromolecules to crystallize in the time available. So if for a certain polymer solution at medium concentration (say about 10 to 20%) crystallization and L-L phase separation should both be possible thermodynamically, then the kinetically slower crystallization process would be surpassed by the fast process of L-L phase separation. The sequence of events might well be changed on increasing the polymer concentration. Then, by increase in polymer supersaturation the rate of nucleus formation for crystallization is increased substantially, while that for the L-L separation stays essentially the same, being more dependent on non-solvent content for its nucleation process.

In figure 2 we have given a schematic representation of the free enthalpy behaviour in the region of high polymer / low non-solvent content of the free component system. One sees that at higher concentrations the free enthalpy of mixing of the solution can be lowered by the formation of solid, crystalline polymer in equilibrium with a solution of a certain lower polymer content. At a lower (or higher) temperature the ΔG_m surface will change its shape and the crystalline polymer will be in equilibrium with a solution of lower (or higher) polymer concentration. The so-called melting point curve for a polymer/solvent pair shows this depend-

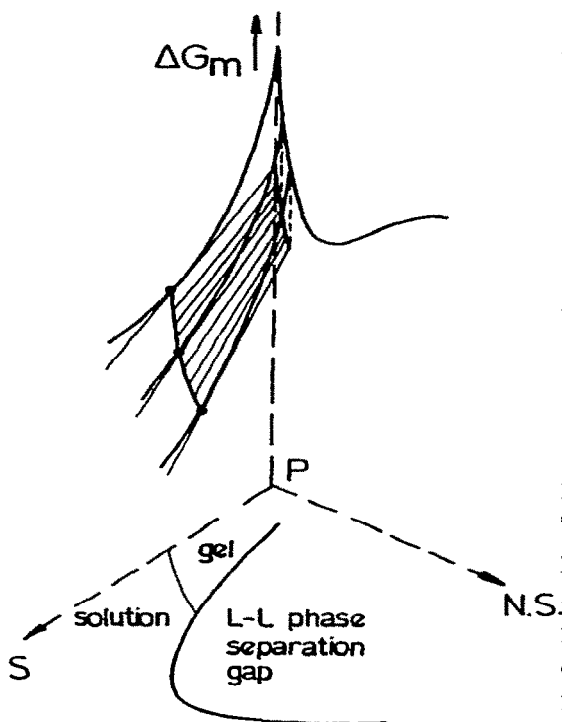


Fig. 2 Free enthalpy behaviour at high polymer - low non-solvent content, explaining the solution - l transition.

ance of melt temperature on composition¹¹⁾.

For crystallization at medium and especially at high concentration, there is a diminished chance to find isolated ordered regions (like spherulites) which have grown out to microscopically observable size. Instead, by the increased rate of nucleation and the limited growth rate, the solution will contain numerous submicroscopical ordered regions, perhaps not larger than the nucleus. These ordered regions act as physical crosslinks in the polymer solution and a thermoreversible polymer gel is formed. Without excluding crosslinks of a different kind to be operative in membrane formation, we think that the type of gelation just described (non-solvent or temperature induced nucleation of ordered regions at high polymer concentration) could

be the leading principle for structure formation in the skin of membranes and for the gelation of pore walls in the substructure.

It is very hard to demonstrate that these gels contain crystalline material, using standard diffraction techniques¹⁶⁾. Calorimetric measurements can be used, however, for studying these thermoreversible gels.

III EXPERIMENTAL

Materials. The polymers used in this work were Cellulose Acetate (CA) Polyacrylonitrile (PAN), Polysulfone (PSn) and Polydimethylphenyleneoxide (PPO). Membranes were prepared as flat sheets, starting from 10-25 weight % of polymer solutions in solvents which are mentioned in the text. The solutions were cast on a glass-plate and immersed in the coagulation bath.

Cloud point measurements. Cloud points were measured using the method described earlier¹⁷⁾. Well degassed (liquid N₂ temperature) solution samples in Pyrex tubes were obtained homogenous by heating at high enough temperatures. These solution samples were then heated or cooled in a thermostat bath at different rates: 1°C per hour,

1°C per 10 minutes or 1°C per 3 minutes, until turbidity appeared or disappeared.

Differential Scanning Calorimetry (DSC). Homogeneous solutions in hermetically sealed sample pans were checked for loss of solvent prior to use. The DSC-apparatus used is a Perkin Elmer type DSC-2

Optical Microscopy. Following the method first introduced by Epstein¹⁸⁾ the phase separation of polymer solutions was examined with an Olympus E.M. Microscope. A drop of the solution is placed between two microscope slides and by means of a syringe non-solvent is introduced near the edge.

Scanning Electron Microscopy (SEM). A high resolution ISI Super III A and a Jeol JSM-U3 equipment were used. Membrane samples were fractured at liquid nitrogen temperature and sputtered with gold with a Polaron and a Balzer sputter unit. Both cross-sections and upper and lower surfaces of membranes were investigated.

IV RESULTS AND DISCUSSION

Koenhen et al¹¹⁾ were the first to show, in their study of a Polyurethane / DMF / water membrane forming system, that there were two distinctly different types of phase separation operative at different compositions:

- L-L phase separation at low and medium polymer concentration and variable non-solvent content and
- gelation at high polymer concentration and low non-solvent content.

Recent work in our group¹⁹⁾ learns that also in the systems cellulose acetate / dioxane / water both types of phase separation could be demonstrated. Curve I in figure 3 shows the cloud points measured at 20°C and curve II shows the solution / gel transition as measured by DSC. Curve I represents a true L-L separation phenomenon: up to polymer concentrations of 20% the cloud points are independent of the rate of temperature change. Cloudiness disappears upon direct reheating at the same temperature at which it appeared on cooling. The phase separated solution can not be separated in two liquid layers: the layer concentrated in polymer is gel-like. With DSC-measurements no heat effect could be observed during cooling; only after aging at temperatures below the cloud points for some time an endothermic heat effect could be detected upon reheating. This latter effect is ascribed to gelation of the concentrated phase after L-L separation has taken place. Curve II is derived from the presence of DSC melting peaks on reheating samples with high polymer concentration (40-55% CA) and rather low content of water. These melting peaks only occur after longer aging times at ambient temperature.

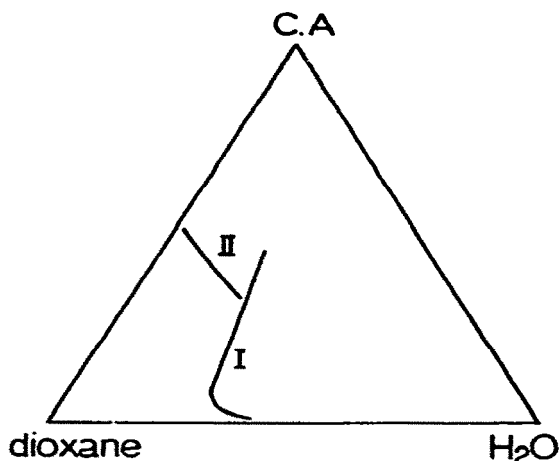


Fig. 3 Ternary diagram CA/dioxane/
H₂O. Curve I: cloud point
curve at 20°C; Curve II:
solution-gel transition.

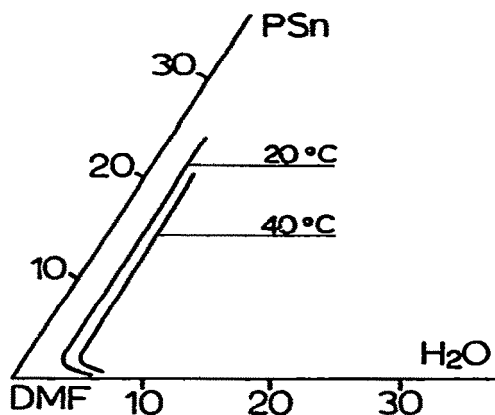


Fig. 4 Ternary diagram of PSn/
D.M.F./H₂O. Cloud point
curves at 20°C and 40°C.

Cooling to lower temperatures (e.g. -10°C) or increasing the water content makes the endothermic peaks show up on immediate reheating.

Figure 4 gives some further evidence of the phase separation types, found in membrane forming system. In this figure the cloud point curves for Polysulfone / DMF / water are given at 20° and 40°C. One sees that only a few percent of water in the solution are sufficient to introduce L-L separation here. We have no direct measurements on gelation yet, but we observe that a PSn solution in DMF, as used for membrane preparation, when stored at room temperature for some hours under exclusion of water gives a precipitate of PSn. Hence the usually employed PSn solutions are on the verge of crystallization (or gelation). From other work²⁰⁾ it is also known that PSn will crystallize from certain solvents. The same observation of precipitate formation on storing is found for solutions of poly 2,6 dimethylphenylene oxide (PPO) in mixtures of trichloroethylene and octanol, from which UF membranes can be prepared¹²⁾. For this system we have done some DSC measurements which clearly show heat effects (crystallization and melting peaks) on cooling and reheating samples, even for the highest scanning rates. Results are well comparable to those reported in reference³⁵⁾ for PPO / toluene.

Phase separation and asymmetric membranes

We will now investigate what can be said about the processes during membrane formation which lead to asymmetric membrane structures. In this discussion we will treat the formation of the skin and of the porous sublayer separately.

Skin formation

The ultimately determining factor for the skin formation is the local polymer concentration in the toplayer of the polymer solution film. This is best illustrated by two completely different techniques of precipitation of membranes from cast films, coined by Strathmann⁹⁾ as

1. precipitation from the vapour phase
2. immersion precipitation

In the first method, long ago developed by Zsigmondy and Bachmann²¹⁾ the precipitation is accomplished at an effectively unchanged polymer concentration in the toplayer, since the vapour phase is saturated with the solvent. Then, by diffusion of non-solvent into the film the only type of phase separation which can take place is L-L separation, giving a symmetric membrane without a skin (see figure 1d in reference 9).

In the immersion technique the solvent depletion from the toplayer of the solution film is extremely fast (diffusion aided by stirring in the bath). An increase in polymer concentration in the toplayer is the result. This increase improves the conditions for the second type of phase separation to occur: gelation. The gelation will be favoured by the penetration of non-solvent. The higher the polymer concentration has become before nucleation in the skin sets in, the more numerous and the smaller will be the structural units, viz the nuclei, because of higher supersaturation.

It will be clear now which factors favour the formation of a dense skin and therefore of a hyperfiltration membrane:

- a higher initial polymer concentration of the solution will favour the conditions for a larger supersaturation in the toplayer before nucleation sets in.
- a lower tendency of the non-solvent to penetrate the toplayer will delay nucleation till sufficient solvent depletion to high polymer concentration has been obtained. A proper choice of non-solvent type and also certain additives to the coagulation bath (salt, glycerin, etc.) will serve this purpose.
- lowering the temperature of the coagulation bath will increase the supersaturation, while at the same time it will decrease the growth kinetics of nuclei formed; a denser skin will result.

A contrary effect, favouring the formation of UF membranes can be found, apart from choosing a lower polymer concentration etc., in the addition of non-solvent to the polymer casting solution. This effect can be explained as follows: one frequently observes that the precipitation concentration for L-L separation in a HF membrane forming system is relatively large about 30% of non-solvent at low polymer concentration being allowed before precipitation sets in, while the precipitation concentration for UF membrane forming systems is often very low, say 5% of non-solvent content or lower; compare for instance CA / dioxane / water in figure 3 with PSn / DMF / water in figure 4 and see also reference 3) and 10). One can then calculate, using well established solutions for this diffusion problem²²⁾ that for the increase in concentration to reach the precipitation value at a certain distance (say 1μ) below the solution surface a difference in time of a factor 5-10 is obtained for the two situations with the HF system taking the longer time. This gives the HF system more time to loose solvent from the top layer. Addition of non-solvent to the casting solution will diminish this effect, increasing the precipitation rate, and favouring the formation of a UF type skin.

Nodular structure of the skin

There is an increasing amount of experimental evidence that the skin of asymmetric membranes consists of spherical aggregates, called nodules, which in a densely packed or perhaps partially deformed arrangement form the selective skin of UF and HF membranes. Most of the data stem from transmission electron microscopy or from scanning electron microscopy^(12, 23-27) but also filtration (water flux) and gas adsorption data are used^{28,29)}. The size of the structural units reported are from 200 to 2000 Å in diameter. Figure 5 obtained with SEM shows for the surface of a PPO membrane (UF) a typical example from our own work. In principle such a nodular structure could be in line with the picture given above for the build-up ordered structural units (nuclei) in the skin layer.

The Porous Sublayer

The formation of the skin will increase the barrier for the diffusion of solvent out and non-solvent into the sublayer of the polymer solution. This means that in the film below the skin, phase separation will take place at much lower polymer concentration compared to that in the skin. For concentrations of the ori-



Fig. 5 SEM-photograph of the nodular surface of a PPO U.F. membrane (slight tilt of the surface under microscope).

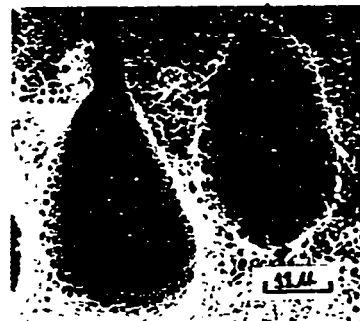


Fig. 6 Cross section of a PSn membrane, showing voids with open walls.

ginal casting composition (or a little higher by solvent loss) this phase separation will be of the L-L separation type as described above in section II-1 and as can be followed by optical microscopy during coagulation.

Two types of structures for the sublayer with clearly different morphologies can be distinguished:

1. sponge structured sublayer
2. conical voids or "fingerlike cavities" in the sublayer

Sponge structure: It will be clear from section II-1 that the pores in the sponge structure are the grown-out nuclei of the dilute phase in the matrix of the polymer solution, which has solidified after L-L separation by gelation at a certain stage. If the concentration of the polymer at the locus where L-L phase separation sets in does not increase too much over the depth of the solution layer, the nucleation density will not vary much over the film thickness and a uniform pore structure will be the result. In order to obtain an "open pore" sponge structure, a certain amount of coalescence, of the drops should occur before the walls of concentrated polymer solution between the pores solidify by gelation. This can be monitored by choosing the proper initial polymer concentration (not too high). A good example of coalescence of small pores with large voids is shown in figure 6 for a Polysulfone membrane.

Conical voids (fingerlike cavities)

A very important feature in immersion-coagulated membranes (in UF membranes as well as in HF) is the presence of the large voids with

a length of several microns to sometimes the total thickness of the membrane. These cavities were first observed in wet-spun fibres³⁰⁻³⁴⁾ The absence of the voids in dry-spun fibres³³⁾ and in dry-RO membranes²⁵⁾ indicates that their formation only occurs in the case of immersion precipitation.

At first it was assumed that the formation was associated with volume changes in the precipitated polymer phase³¹⁾. Later Graig³⁰⁾ proposed the mechanism of penetration of non-solvent through defects (cracks) on the surface of the spinning filament. The same mechanism in the case of immersion coagulated membranes was proposed by Strathmann⁸⁾. In a systematic study of the kinetics of void formation in PAN fibre spinning Gröbe³²⁾ came to the conclusion that diffusion of both solvent and non-solvent to certain areas was the basis for void formation. In our opinion the available experimental data are consisted with this mechanism. Some typical facts remain interesting for a further consideration:

- through optical microscopy one observes that the voids move inward faster than the - diffusion controlled - coagulation front.

- the boundary of the voids does not solidify by gelation during its growth, since coalescence with small pores remains possible (figure 6).

- often the growth of the void slows down and the coagulation front for L-L separation passes beyond the lower end of the cavity.

The main driving force for the growth of the void is the decrease in free enthalpy (ΔG_m) upon mixing solvent and non-solvent in the void. This ΔG_m decrease should be so large that it can compensate for a possible increase in ΔG_m when solvent is depleted from the polymer solution surrounding the void. The situation is best illustrated by following the arrows in figure 1 at point X (large decrease in ΔG_m if non-solvent mixes with solvent) and at point Y (increase in ΔG_m when a polymer solution becomes more concentrated). The general mechanism can be described as follows:

- when the skin is formed, non-solvent penetrates into the underlying polymer solution faster at certain spots in the skin (e.g. a thinner part of the skin or a local loose arrangement of the structural units, giving a more favourable pathway for diffusion); only in systems with a large driving force for solvent / non-solvent mixing this heterogeneous type of nucleus is formed.

- solvent diffuses from the surrounding polymer solution to these statistically spread loci and a gradient in concentration ranging from practically pure solvent (near the interface of this area with

the polymer solution) to non-solvent (near the skin surface) is set up; there is a fluid interface between the polymer solution and the void.

- because mass transfer in the void is faster than through the polymer solution phase, the void may grow faster initially than the moving coagulation front proceeds; at a certain point however, the driving force for solvent transport may fall short because of decrease in gradient.

It is emphasized that the contents of the void during growth is not in equilibrium with the surrounding polymer solution, in the sense of L-L separated binodal phases. It is clear that after the void stops growing, normal L-L type phase separation takes place in the polymer solution surrounding the void and in front of it. A proof that the void / solution interface stays fluid during cavity growth is given by all those systems where we find in the membranes cavities with open walls (see figure 6).

Our observations are in conceptual agreement with the earlier proposed mechanism by Gröbe^{3,2)} and with results on the effect of important monitoring variables to prevent void formation (see Frommer^{3,4)} and Strathmann⁵⁻⁹⁾ such as:

- lowering the tendency of non-solvent to penetrate into the casting solution (T, salt addition to non-solvent, solvent / non-solvent pair with smaller affinity).

- increasing the skin thickness or the density of the skin (see above in this discussion).

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