Energy dependent polymerization of resin-based composites
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Appendix 2

Reconciling The Bulk ECR With the Thin Film ECR

Initial investigations (Chapter 3) utilized a thin film technique to determine conversion of RBC. This methodology has flexibility in being able to follow conversion with time. The ECR obtained with this technique, however, does not accurately describe the conversion within an RBC at depths where the energy levels are low. The ECR obtained with bulk cured RBC (Chapter 4) does give accurate conversion information within the RBC material, even at depths where the light energy is very low. To compare the two forms of ECR, they need to be placed on an equal basis regarding the energy scale. The thin film ECR described in Chapter 3 was based on energy output of the light source, while the bulk ECR described in Chapter 4 uses the actual energy within the RBC. By correcting for reflectance losses that pertained in the experimental set-up, the thin film ECR can be displayed on the same energy scale as the bulk ECR, as shown in Figure 1.

![Figure 1](image)

It can be seen (Figure 1) that below an energy density of about 1000mJcm\(^{-2}\) the thin film method predicts a lower conversion than is predicted by the bulk ECR. The actual conversion within the RBC is significantly greater below this exposure level. However, the bulk ECR is not accurate at the very top surface of the cured RBC. Specimens taken from the top surfaces of polymerized cylinders, exposed to varying energies, were examined by the same micro FTIR methods described in Chapters 4 and 5. The relationship between energy and conversion for
this top surface is shown in Figure 2 where it can be seen to agree with the thin film ECR.

![Figure 2. Fractional conversion of specimens dissected from top of bulk-cured samples covered with polyester film compared to ECR's depicted in Figure 1.](image)

The most likely reason for the difference between the bulk ECR, which describes conversion within RBC, and the other two relationships is oxygen inhibition of polymerization. It has been observed in hardness testing that the maximum hardness occurs at some small depth below the surface when RBC is cured in air [1]. Covering with a polyester matrix was shown to increase surface hardness but not to the extent of curing in a nitrogen atmosphere. Hence, both the outer surface of bulk specimens and thin films are likely to be subject to oxygen inhibition that cannot be overcome at low light energies. Above around 1000 mJcm\(^2\) it is presumed that the amount of oxygen present in the thin film or the outer surface is overwhelmed by sufficient generation of free radicals that there is no effect on conversion.