Pulsed Electron Beam Curing of Polymer Coatings

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Pulsed electron beam (PEB) curing is significantly more energy efficient and speedy than continuous EB curing, as Weiss and Dunn (2002) showed in a pioneering work. It exploits the inherently heterogeneous nature of energy deposition along electron tracks to compartmentalize free radical initiation sites, thereby suppressing second-order termination reactions in favor of first-order propagation. Appropriately timed pulses thus allow heterogeneous polymerization in a single phase, enabling in-line curing of polymeric coatings from monomers at relatively high process speeds. That is beyond the capabilities of conventional electron beams.

A nanoscopic view of the process reveals how PEB can selectively support first-order reactions. In that view the mean field approximation that underlies standard chemical kinetics breaks down and the concept of electron track structures is central. The deposition of energy into matter along electron tracks is heterogeneous: energy is transferred from the impinging electrons in discrete, localized interactions, so-called spurs. The resultant reactive species in each spur initiate free radical polymerization reactions that eventually are terminated by way of reaction-diffusion.
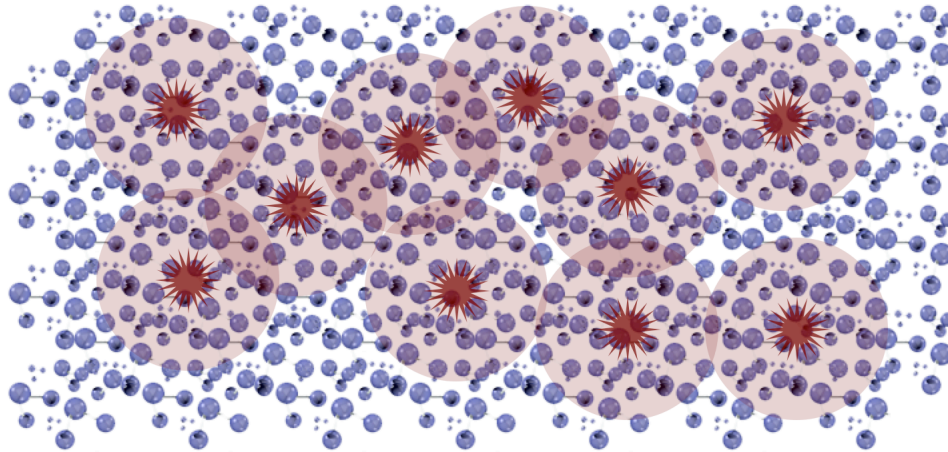

Figure 1: Schematic representation of spurs in aqueous medium. During well-timed pulses spurs do not overlap initially, leaving time for first-order propagation reactions to proceed before termination is possible, as indicated by shaded volumes around spurs, through which growing radical chains have to grow to meet each other. Drawing is not to scale, spur separation would be much larger.

Whereas each spur created during a single pulse has a diameter of only about 18 nm under typical PEB operating conditions, it occupies a volume more than 100 times that size. This leaves ample space for first-order polymerization to proceed before radicals meet to terminate each other. Thus, the spatial distribution of spurs creates a temporal delay during which no termination can take place. This differs from continuous EB exposure, during which this highly productive, termination-free phase of the process is cut short by excessive initiation, which leads to spur overlap and thereby swamping by termination reactions. Theoretical computations of conversion kinetics based on prior analysis by Wen and McCormick (2000) of the kinetics of pulsed ultraviolet (UV) curing that included the fall of species mobility with rising conversion, which can lead to radical trapping, confirms the benefits of PEB.

To test this view, a PEB apparatus that can operate in the desired regime has been custom-built at the University of Minnesota, succeeding the now-defunct prototype used by Weiss and
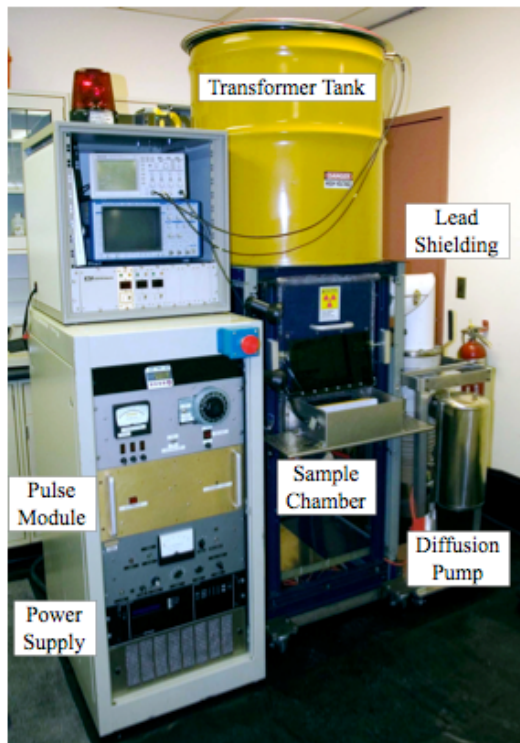
Dunn (2002). A picture of the new system is shown to the left. Its unique features include an inerted, temperature-controlled 200 cm^2 sample chamber at atmospheric pressure with uniform exposure to 80–160 kV electrons in pulses of 5–20 µsec duration at frequencies of up to 2 kHz. This allows wide-ranging investigation of PEB curing, currently in progress. Experimental results apply directly to industrial web widths, and it appears that equipment design can be readily extended to large facilities.

We have investigated conversion kinetics in acrylate systems to benchmark PEB curing against continuous EB and UV curing. Pressure-sensitive adhesives, built from monofunctional acrylates such as 2-ethylhexyl acrylate (2-EHA), are converted dramatically faster and more completely by PEB. The observed changes in properties with changes in operating parameters are consistent with predictions from the kinetic model. Conversion data of other mono- and multifunctional acrylate systems benchmark PEB curing against continuous EB and UV curing, quantifying process improvements and delineating the useful operating ranges of pulsed EB curing. Exposure of di- and trifunctional acrylates to pulsed EB compares favorably to UV curing because less energy and no photoinitiators are needed for similar conversions.
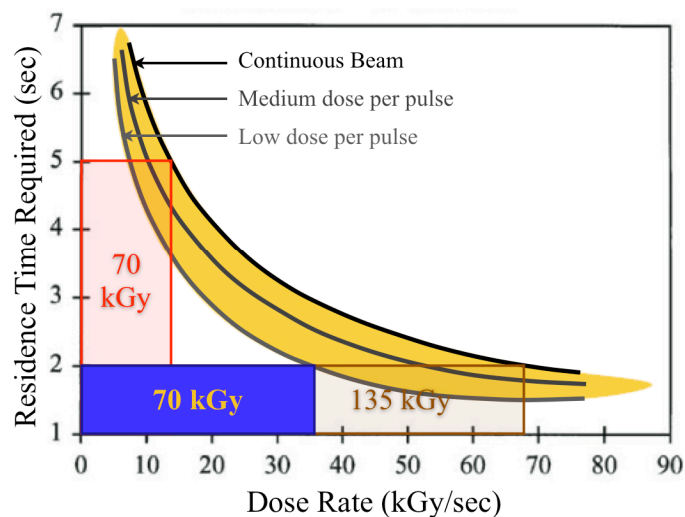
Figure 2: Summary plot of available data for 2-EHA (adapted from Weiss and Dunn, 2002). Shown schematically are the residence times required to achieve a target conversion as a function of average dose rate, which is the product of dose per pulse and pulse frequency. Lowering doses per pulse allow for short residence times without large energy penalties, which is not possible with a continuous beam. The total energy requirements for operating points on the continuous and pulsed curves are indicated by the areas of the rectangles they define.

For reducing overall energy requirements, improving process speeds, and obviating the need for photoinitiators, pulsed EB curing should thus be considered the radiation curing method of choice for many future applications.

References:

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