

REACTIVE OLIGOMERS: THE KEY COMPOUNDS OF THE
NEXT YEARS RADIATION CHEMICAL TECHNOLOGY

T.Czvikovszky, E.Takács, I.Czajlik

Research Institute for the Plastics Industry
H-1950 Budapest, Hungary

ABSTRACT

The reactive oligomers containing unsaturated double bonds in their chain of limited length are playing a predominant role in the radiation crosslinking, coating and composite processing as well. Radiation-reactivity of different oligomers is compared at very high dose-rates up to 800 kGy/sec.

KEYWORDS

EB curing of coatings, composites, crosslinking, radiation-reactive epoxy-acrylates, polyesters, dose-rate dependence of conversion.

RADIATION-REACTIVE OLIGOMERS

The advanced radiation curing technology has created and is consuming every year a growing amount of specific reactive oligomers. The world-market of the UV/EB reactive oligomers was more than 30 kt/y in 1987, and seems to grow at an annual rate of 15 % /1/. The most important radiation-reactive oligomers contain ester-, urethane- and epoxy-groups in their main chain terminated with acrylic or methacrylic end-groups /2/. Epoxy-acrylate and urethane-acrylate oligomers are dominating actually the most applications in Japan and USA, but polyester-acrylates are the most used ones in Europe /1/. The choice of different reactive oligomers is however much broader. Reactive oligomers can be prepared by attaching acrylic functionality onto natural oligomer backbones producing e.g. epoxidized and subsequently acrylated natural oils, acryl-amidomethyl-starch, acryl-amidomethyl cellulose, etc./3/ Acrylated polybutadiene oligomer can be considered as a radiation reactive rubber pre-polymer /4,5/. Even the century-old novolac and melamine resins can be involved in radiation curing if epoxidized and then acrylated /4,6/. N-vinyl caprolactone and his oligomers are also radiation-reactive, similarly to the polyamid acrylates/7/. Contradictory requirements can be brought together in radiation-reactive oligomers. Silicones, embodying inertness and release-functions, if modified with appropriate acrylic groups, became EB-reactive still conserving enough inertness and release-functionality when radiation-cured /8,9/. Recently epoxysiloxanes have been introduced for radiation crosslinking /10/. Fluorine containing polyols introduced into radiation curable oligomers result in excellent new materials for telecommunication /11/.

The chemistry sections of recent conferences on polymers and radiation technology are demonstrating that along this pathway a growing number of taylor-made oligomers can be produced /1,3,5,6 .../. These are highly functionalized, prefabricated elements which can be built in by radical chain reactions in different crosslinked or composite structures, not only in coatings. On the other side, these three fields of application - crosslinking, coating and composites - are the most dynamically growing ones of radiation processing.

Radiation crosslinking in presence of reactive additives can be expanded well beyond the polyethylene. Other polyolefines such as PP, EVA, EPDM, CPE, CSPE etc.; halogen containing polymers as PVC, PVDF, PVF and other fluoro-polymers; different polyamides, siloxane elastomers and many others are radiation crosslinkable applying such "enhanced crosslinking" methods /12-15/. Theoretical possibilities are almost illimited, but technical feasibility is controlled very much by miscibility and compatibility of the components in the blend during the pre-irradiation phase of technology. Low molecular crosslinking agents have greater chance to emigrate, sweat out from the blend before the radiation crosslinking. Reactive oligomers of adequate molecular mass, polarity and compatibility are the key-compounds of the expanding application of radiation crosslinking in the field of elastomers, cable-jacketing, technical tubes, hoses, and plastics products in general.

Composite processing by radiation similarly depends very much on reactive oligomers. Pre-mixed raw materials of fiber-reinforced plastics such as BMC /Bulk Moulding Compound/ SMC /Sheet Moulding Compound/ or prepregs of fiber-reinforced plastics can also be radiation processed /16-18/. Viscosity, and generally the rheological properties of the binder is determining mostly the final properties of the glass fiber- or carbon fiber-reinforced systems. Reactive oligomers and oligomer-monomer mixtures with adequate viscosity, flow, wetting, adherence and other functional properties before and after radiation curing are the key compounds of composite making as well.

EFFECT OF OLIGOMER REACTIVITY

The radiation-reactivity of different oligomers in some modell-mixtures for EB-curable coatings is compared in the followings. The oligomers have been synthesized in our laboratories, as described elsewhere /19,20/.

Although apparently epoxy acrylates and urethane acrylates dominate the field of radiation curing, radiation reactive unsaturated polyesters /UP/ still have an important share of the UV/EB curable oligomer market. Our UP-K is a chemically resistant type of UP, made for EB curing. On the Fig.1. the conversion of a mixture /50:50/ of UP-K with hexane-diol-diacrylate is monitored by measuring the pendulum hardness in function of the dose-rate. The dwelling time under the EB is determined by the conveyor speed "c" /m/min/ and the absorbed dose "D" /kGy/ can be calculated from the beam current /I, mA/ and a constant "k"

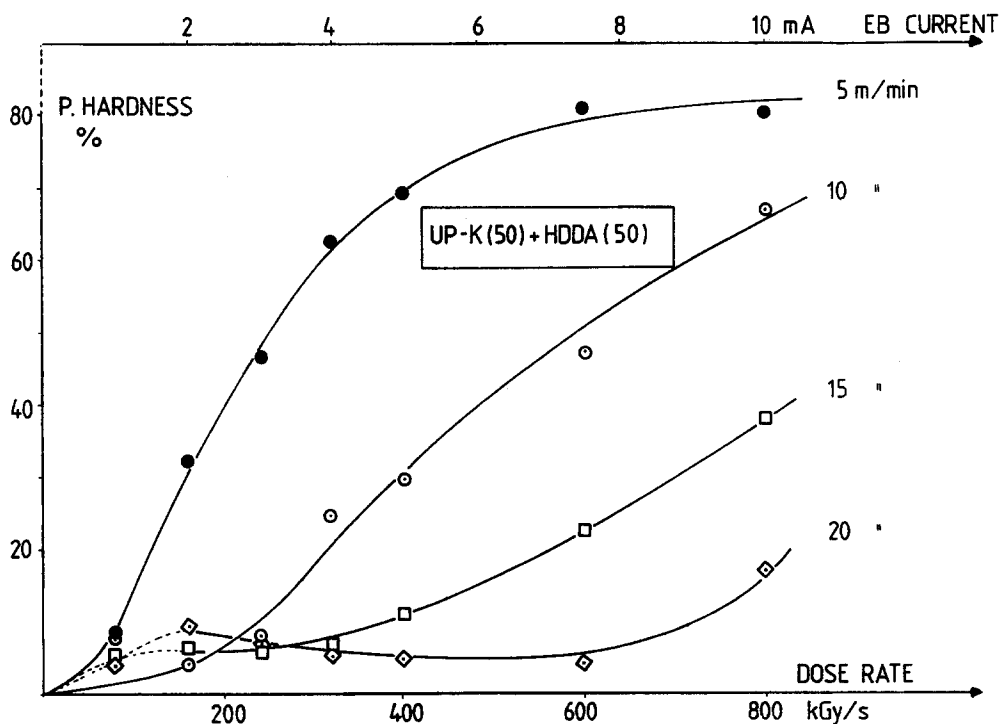


Fig.1. EB-curing of a mixture of unsaturated polyester UP-K and hexane diol diacrylate HDDA /50:50 wt%/ in function of dose rate at different conveyor speed /5-20 m/min/ of an ELECTROCURTAIN 150/15/180 Lab unit. Inerting: 300 ppm O_2 in Argon.

characterizing our ELECTROCURTAIN CB 150/15/180 L according to the formula $D = k \cdot I / c$ where $k=196,2 \text{ kGy/mA} \cdot \text{m/min}$. In another study [21] we investigate the effect of monomer moiety by changing the monomer and maintaining the oligomer. In the present work we compare the reactivity of oligomers. On the Fig.2. we show another reactive oligomer-ester UP-R which is producing more flexible, crosslinked network and which is higher in his reactivity.

The radiation-response of such an oligomer-monomer system is reflected by pendulum hardness only indirectly. The hardness of a quite elastic coating layer of about $50 \mu\text{m}$ thickness as compared /in %/ to the reference glass surface - is far from describing conversion of the coating into crosslinked gel. After a time-consuming extraction in hot toluene the remaining gel content of the same samples are seen on Fig.3.

It is clear on the upper three curves of Fig.3. that at conveyor speeds of 5-10-15 m/min and 100-300 kGy/s dose-rate, an absorbed dose of about 50 kGy results in about 90 % of crosslinking which is almost satisfactory for any practical purpose if we assume a spontaneous after-cure. Comparing these data with that of Fig.2. it can be seen that at those dose levels the pendulum hardness values were less than 40 %.

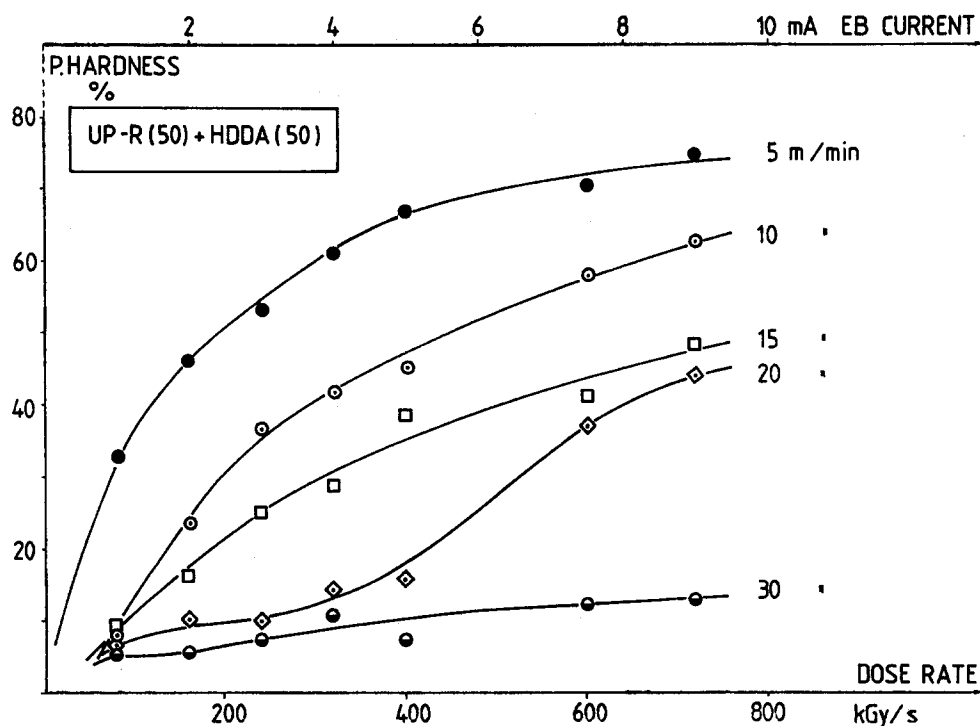


Fig.2. EB-curing of a mixture of UP-R and HDDA /50:50 wt%/ in terms as on Fig.1.

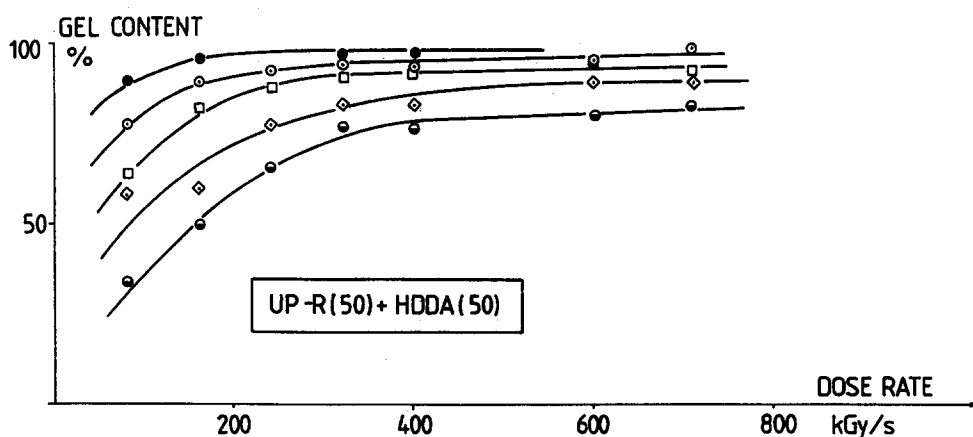


Fig.3. Gel content of EB cured coating samples of Fig.2. in function of dose-rate, at different conveyor speeds /symbols as on Fig.2./

It is of high practical importance to know the exact dependence of curing dose on the dose-rate [22]. We are not able to describe in correct mathematical formula the dependence of the overall rate of polymerization - proceeding in a fraction of second - as a function of the dose-rate. However, the above data monitoring the hardness and gel content are enough to characterize such dependence at some interim, near to complete conversion. Fig.4. shows the dose levels, taken from Fig.2. where hardness reaches 50 % /D_{H-50}/ or

40 % $/D_{H-40}/$ in function of dose-rate, both in logarithmic scale. Fig.5. shows similar picture for dose levels required for gel content of 75 % and 60 % $/D_{G-75}$ and $D_{G-60}/$.

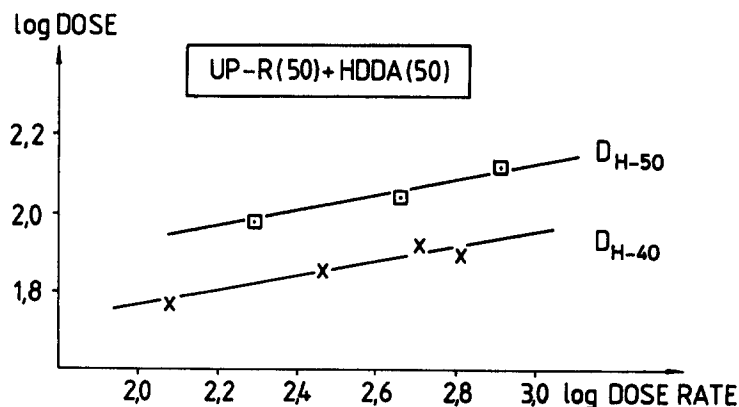


Fig.4. Dose required to reach 50 % and 40 % of pendulum hardness $/D_{H-90}$ and $D_{H-40}/$ in function of dose-rate, for the system UP-R/HDDA described on Fig.2.

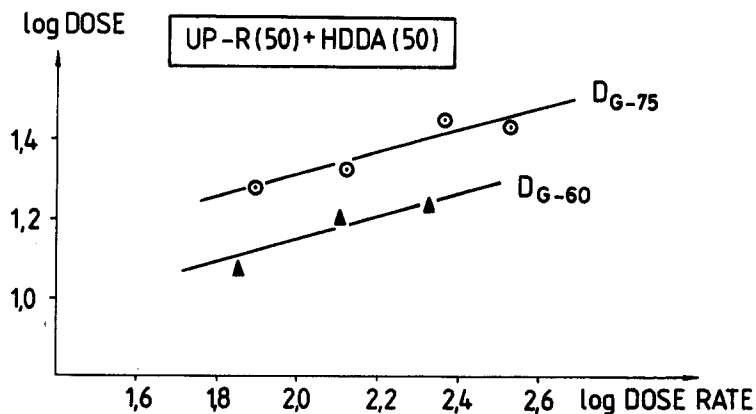


Fig.5. Dose required to reach 75 % and 60 % of gel content $/D_{G-75}$ and $D_{G-60}/$ in function of dose-rate for the system UP-R/HDDA described on Fig.3.

Similar to our earlier work [20] these curves on Fig.4. and Fig.5. are showing a weak dependence with a slope of + 0,2 in case of a UP/HDDA, coating system of still limited EB-reactivity.

In the followings again a higher reactivity oligomer, an aromatic epoxyacrylate /EPA-B', synthesized by us/ was studied with the same HDDA monomer. On the Fig.6. it is seen that acceptable hardness values can be reached with doses below 50 kGy even at higher conveyor speed. The dose required to obtain 70 % and 50 % hardness in function of dose-rate /both in logarithmic scale/ is presented on Fig.7.

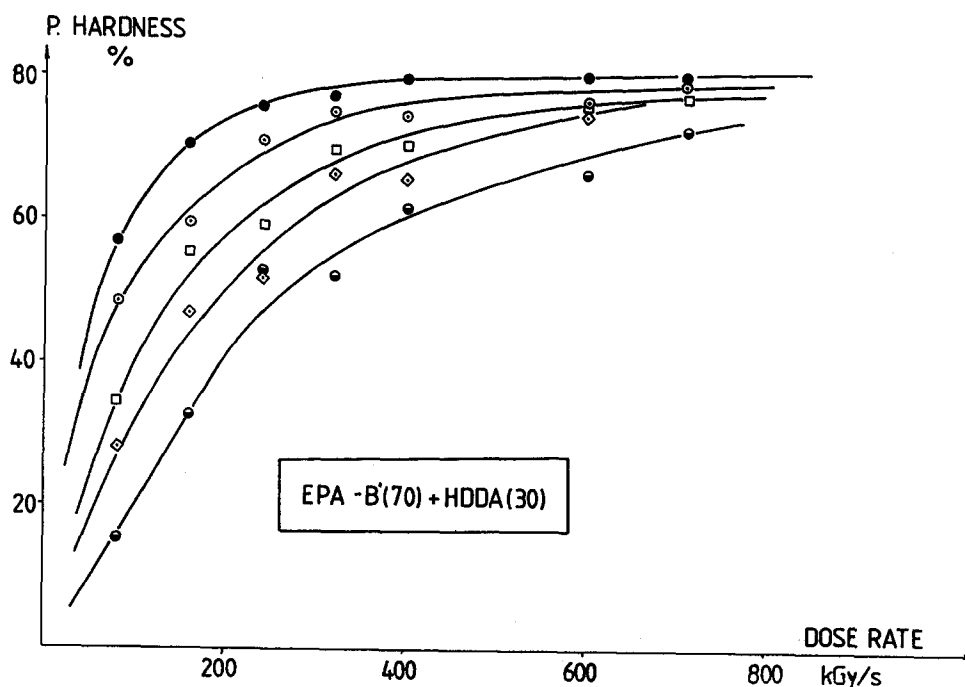


Fig.6. EB-curing of a mixture of aromatic epoxy acrylate EPA-B' and HDDA /70:30 wt%/ in terms as on Fig.1.

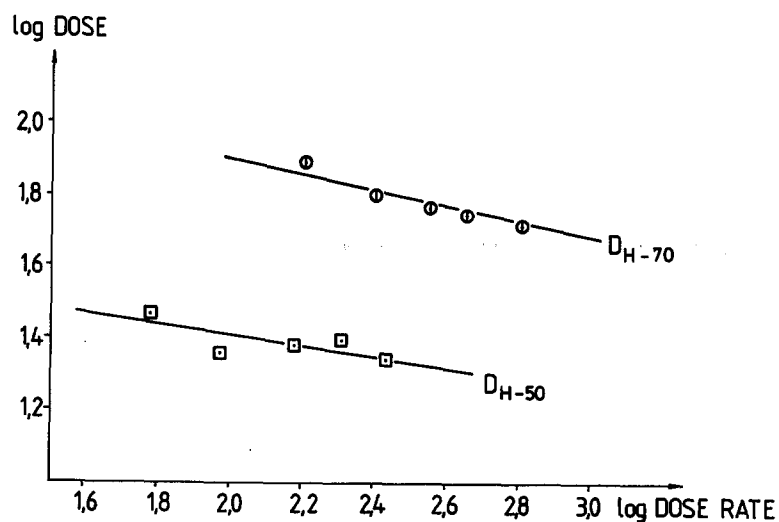


Fig.7. Dose required to reach 70 % and 50 % pendulum hardness / D_{H-70} and D_{H-50} / for the system EPA-B/HDDA presented on Fig.6.

Discussing the dose requirement data in function of dose-rate, we have to state that differences in oligomer reactivity are greatly affecting the rad.-response of the system. With adequate modifications unsaturated polyesters are still acceptable in their EB-reactivity, to be used as component of taylor-made binders of specific features /crack-resistance, elasticity, etc./. The curing dose as a function of dose-rate is the most important variable in the

EB-curing technology. Earlier literature data /23,24/ considered the polymerization rate to be independent of the dose-rate above 3 kGy/s. We found a slight but significant dependence, differing however in trends for limited reactivity UP and for high reactivity EPA.

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