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Radiation Curing in Coatings

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Abstract. The market for radiation curing in coatings exhibited a significant continuous rise during the past decades. A rough overview over curing mechanism, coating formulation and raw materials is given. EB-Coatings for hardboards and UV-coatings for optical fibres are described more detailed as examples for application.

1. Introduction

The market for radiation curable coatings showed a significant continuous increase during the past decades, future outlooks are promising. There are a number of reasons for this successful growth. First radcure coatings need less (if any) additional solvents than conventional coatings, thus being of ecological interest. Second this coating technology exhibits a number of economical advantages: compact installations, high productivity because of high speed curing, savings in materials because of excellent film properties of the coatings even in thin layers. And last not least savings in energy compared to conventional heat curing coatings can be realized, because energy is only needed to initiate curing.

Principles of Electron Beam- and UV-Curing

Radiation curable systems nowadays are usually based on radical curing mechanisms, this is true for EB-curing in all cases and for UV-curing in most cases [1].

While the electron beam is able to generate the radicals needed to initiate curing, UV-curing needs a photoinitiator which starts the curing process. Upon curing the process follows the mechanism of a radical polymerisation (*Scheme 1*).

2. Radcure Coatings – Formulations

In order to get applicable coatings with the tailored properties wanted coating formulations are mixed using different types of raw materials which will be introduced in the following (*Scheme 2*) [1].

2.1. *Resins and Oligomers*

In general for radical cure mechanisms resins and oligomers containing C=C bonds are used. Such types of resins are well known and for instance unsaturated polyesters containing maleic acid groups are used in coatings technology for many years. In combination with photoinitiator and styrene as a reactive diluent these unsaturated polyesters were the first systems for UV-curable coatings applied on wood materials.

For nowadays applications these older systems unfortunately are too poor in reactivity so new types of highly reactive resins were developed.

These highly reactive resins are derivatives of types of resins well known in coatings. Based on polyurethanes, polyesters, polyacrylics, or, latest, on polyethers new products were created by introducing acrylic groups. The acrylic group is distinguished by its high reactivity compared to other unsaturated groups like methacrylic groups or compared to styrene.

The resins are usually diluted with reactive monomers in order to get applicable coatings with sufficient low viscosity. As the monomers used are often toxic coating formulations afford very careful handling. Therefore, the development in radcure coatings is focussed on resins with very high reactivity and low viscosity longing for formulations without any reactive monomers. On the other hand these new low viscous resins exhibit a more oligomeric character, thus they may have to be classified concerning their irritation potential and other relevant ecological properties.

2.2. *Reactive Monomers*

In order to adjust radcure coatings to all the possible industrial applications reactive monomers are used to regulate the

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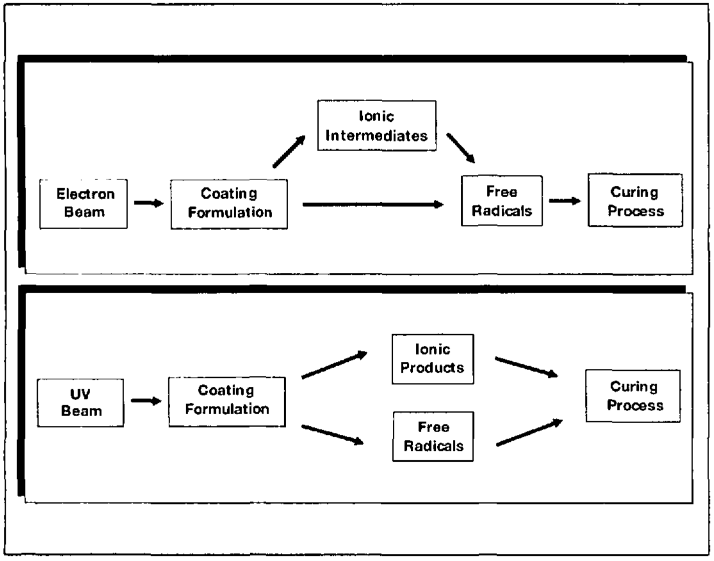
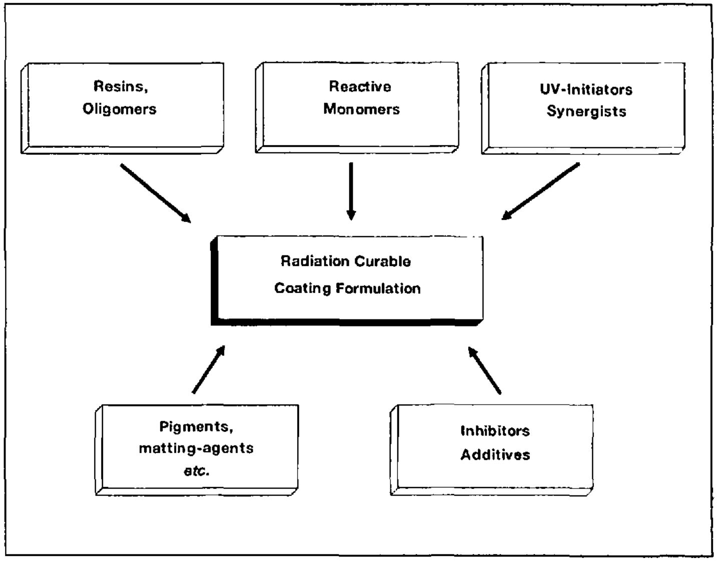
Scheme 1. *Process Pattern of UV- and EB-Curing*



Scheme 2. *Pattern of Coating Formulations*



viscosity and the reactivity of the lacquers. The most common type of reactive monomers are derivatives of acrylic acid, sometimes combined with other types of monomers like *N*-vinylcaprolactam or *N*-vinylpyrrolidone.

Monofunctional monomers are chosen if flexible or elastic coatings have to be achieved. Difunctionals like hexanediol diacrylate or polyfunctionals like trimethylolpropane triacrylate are chosen if rigid and scratch resistant coatings are desired.

The matching of the combination of resin and monomers is the key point in formulating a coating regulating the basic properties of the resulting film.

2.3. *Photoinitiators and Synergists (UV)*

UV-curable coatings need photoinitiators to start polymerisation. There are two different types of initiators (*Scheme 3*). In one type of initiators UV-light leads to an intramolecular cleavage of bonds resulting in high reactive fragments that start curing.

The other group of photoinitiators like benzophenone needs additional synergists. In this group UV-light only leads to an excited state of the initiator molecule which then generates reactive radicals by intermolecular hydrogen transfer. Hydrogen donors used as synergists are *e.g.* amines or alcohols.

2.4. *Inhibition by Oxygen*

Inhibition by oxygen is a fundamental problem in radcure coatings. Oxygen reacts with the radicals generated by radiation on the film surface, turning high reactive radicals into low reactive species which suppress curing. The result is a sticky film surface with insufficient properties. In UV-curing this effect is not as dramatic, the concentration of free radicals is usually high enough to overcome the influence of oxygen. In EB-curing inhibition by oxygen leads to the necessity of working under inert gas, usually nitrogen.

2.5. *Additives*

Additives are used to regulate a lot of properties additional to the basic properties given by the composition of resin, monomer, and initiator. As the radiation induced polymerisation leads to a significant shrinkage of the coating often problems in adhesion to the substrate occur. In order to overcome this effect additives to improve adhesion are added to the coating formulation.

Other types of additives regulate *e.g.* gloss (matting agents), levelling or viscosity (thixotropying agents).

3. Application

In the market for radcure products UV-technology and EB-technology are competitors. Nowadays this market is dominated by the UV-technology. One reason for this definitely is the more expensive equipment of the EB-technology, also UV-technology usually does not need inert gas and the coating of three dimensional shaped substrates is possible. But beside this EB-technology offers a number of advantages, so EB-curing does not need initiators and the curing of pigmented systems is possible without problems. Also curing of thick films up to 0.5 mm can be done, while UV-curing usually is limited to film thicknesses below 0.1 mm.

UV-curing found its application *e.g.* in the markets for wood finishing, paper upgrading, printing inks and some special fields like optical fibre coatings [2]. EB-Curing is used for wood finishing (direct competitor to UV), cosmetic packaging, siliconisation, casting papers and more.

In the following wood finishing *via* EB-technology and optical fibre coatings *via* UV-technology will be presented more detailed as examples for both types of radcure applications.

3.1. *Electron Beam Curing: Example Wood Finishing*

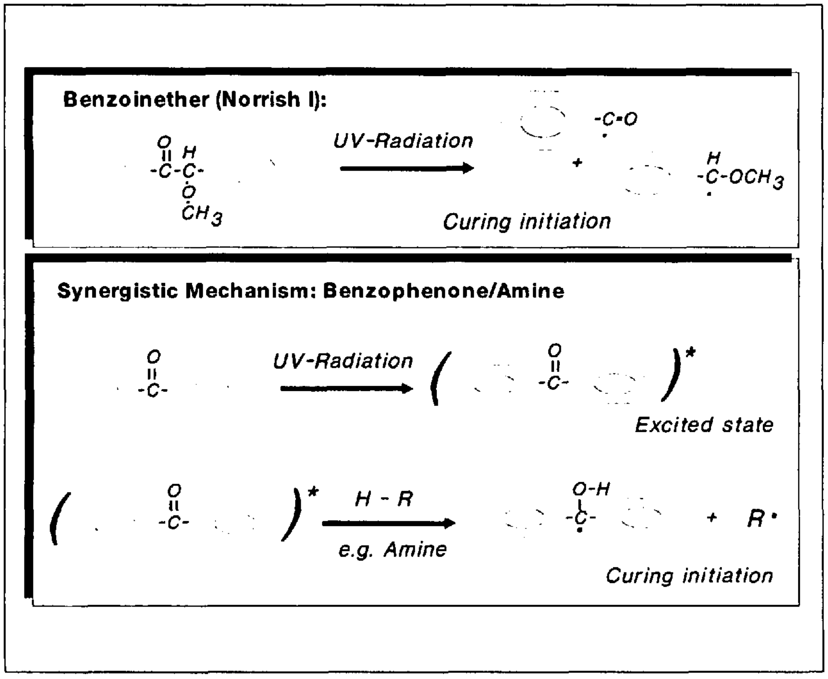
In *Figs. 1–3* three fundamental parameters of EB-curing are shown: what energy is needed to get sufficient curing (*Fig. 1*), what energy is needed to cure the coating from surface to bottom (*Fig. 2*) and what is the highest energy level possible without decomposition of the film surface (*Fig. 3*).

Before any application, these parameters have to be fitted to the applied system.

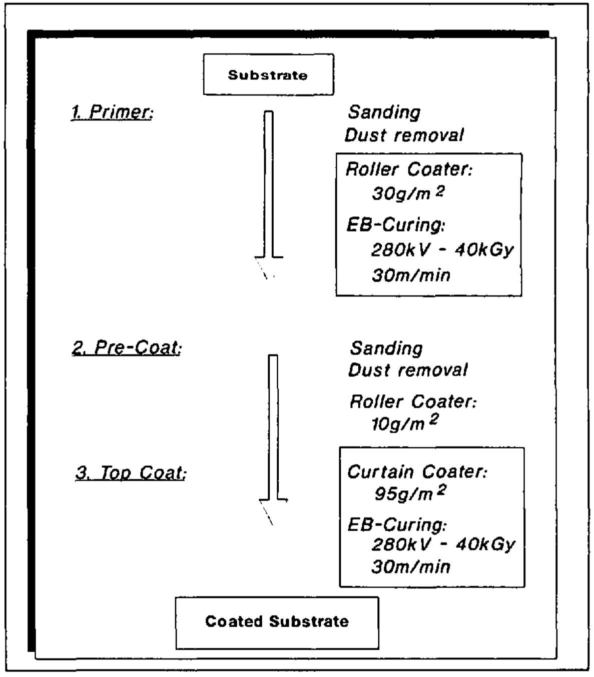
Wood finishing is one of the main application fields for EB-curing. Using the example of hardboard finishing EB-cure coating systems will be discussed.

Relevant properties for this special kind of coatings are chemical resistances against a number of different substances, *e.g.* water, acetone, acetic acid, coffee, tea, *Coca Cola*, lipstick, and more. The different specifications are given in DIN 68861. Another property of importance is observed by a cold check test. In this test the coated substrate is held 4 h at –20° imme-

Scheme 3. *Examples for Photoinitiators Used in UV-Curing*



Scheme 4. *Process Pattern for Coating Hardboards*



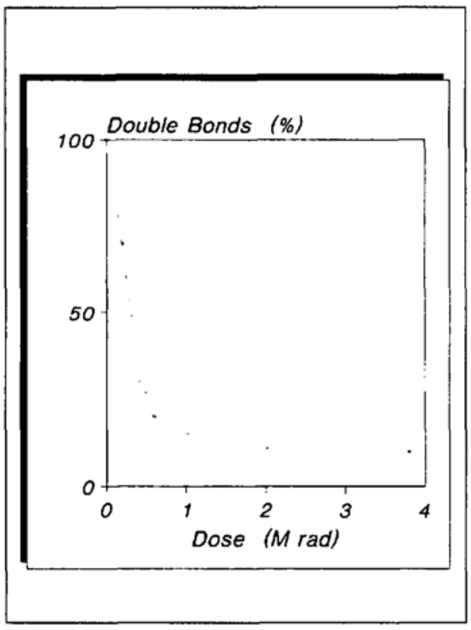


Fig. 1. *Residual double bonds* vs. *dose*

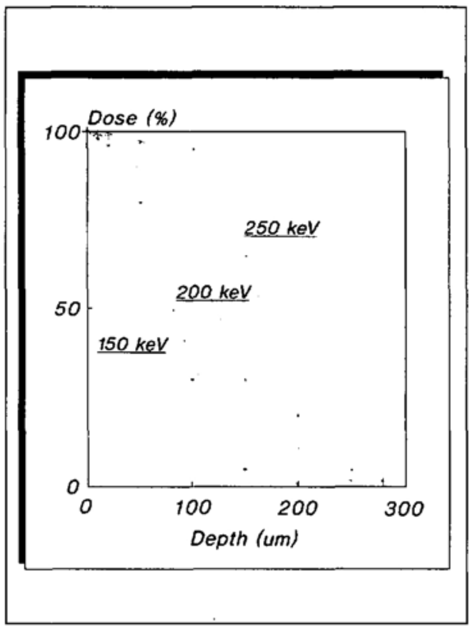


Fig. 2. *Dose/depth profile*

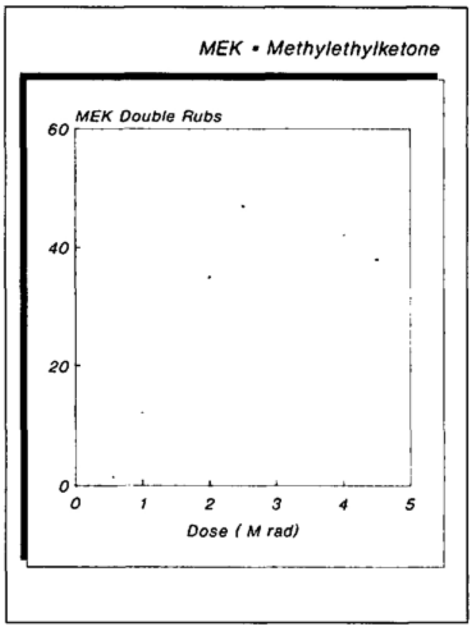


Fig. 3. *Solvent resistance (ethyl methyl ketone)* vs. *dose*

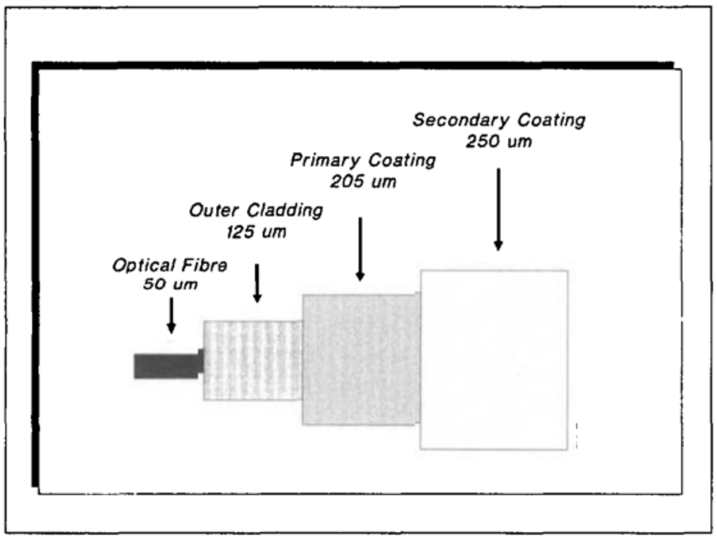


Fig. 4. *Optical fibre – dual coated*

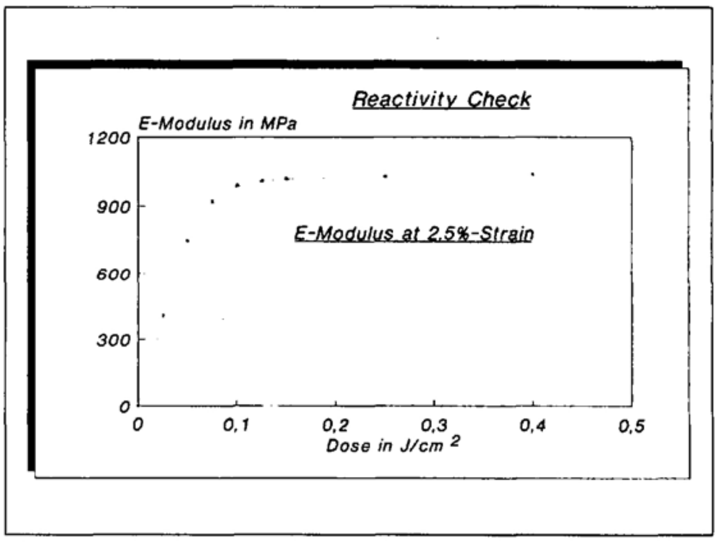


Fig. 5. *Reactivity check: E-modulus* vs. *dose*

diately followed by 4 h at 60°, running 45 cycles of this procedure. The coating has to fit this without any decrease in quality. Other tests on the coated substrate check *e.g.* adhesion, light stability, scratch resistance of the coating. All these specification tests can be passed with special EB-cured coating systems. The general process pattern for the coating of hardboards is given in *Scheme 4*.

In a first step a primer is applied and cured. This primer is responsible for sufficient adhesion to the substrate and it also has to compensate roughnesses on the substrate surface. In a second step a thin layer of a pre-coat is applied to bind residual dust and to nivellate small unevenesses of the primer surface followed by roller coating with the top-coat. Pre-coat and top-coat then are cured together resulting in the coated end product.

As the different layers of the coating have different requirements to fulfill, coating formulations for these different layers have to be differentiated: while in the primer the content of filling materials is up to 43% this content decreases in the upper layers being less than 10% in the top-coat. On the other hand pigments and difunctional monomers are incorporated in much higher amounts in the top-coating, both being responsible for the appearance of the coating surface. The different requirements are also mirrored in the used resins. In the primer a highly flexible acrylated epoxy resin is incorporated while in the top-coating less flexible resins are used, giving hard and scratch resistant surfaces.

3.2. *UV-Curing: Example Optical Fibre Coatings*

Lightwave data transfer based on fibre optics is a technology which enabled an increasing efficiency of telecommunication within the last decade [3][4]. Bundles of discret fibres are used in the field of telecommunication over long distances. The fibres can be chosen from a wide range of types. The most common configuration is a core of silica, doped with oxides of Ge or P to raise the refractive index, a cladding of pure silica and an organic coating which usually consists of two layers (*Fig. 4*). The fibre surface is protected by an on-line process immediately after it has been drawn from a preform [5]. Beside the protection of the fibre surface towards moisture, which could lead to hydrolysis and micro-cracks, the main function of the coating is to minimize signal losses due to microbending. This term refers to random bends induced by lateral forces on the fibre or by thermal fluctuations causing axial stress. These random bends are able to interact with the optical modes in such a way that they leave the core [6]. In order to decrease these negative effects the fibre is surrounded by a dual coat, consisting of a soft

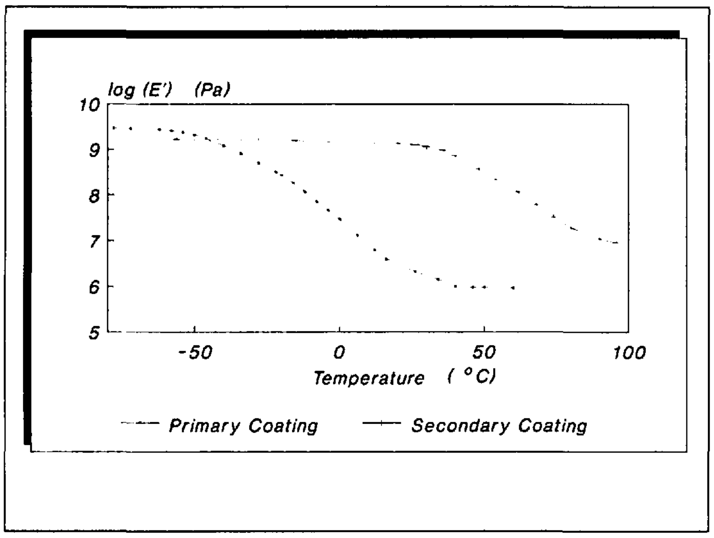


Fig. 6. *Tensile modulus E'* vs. *temperature*

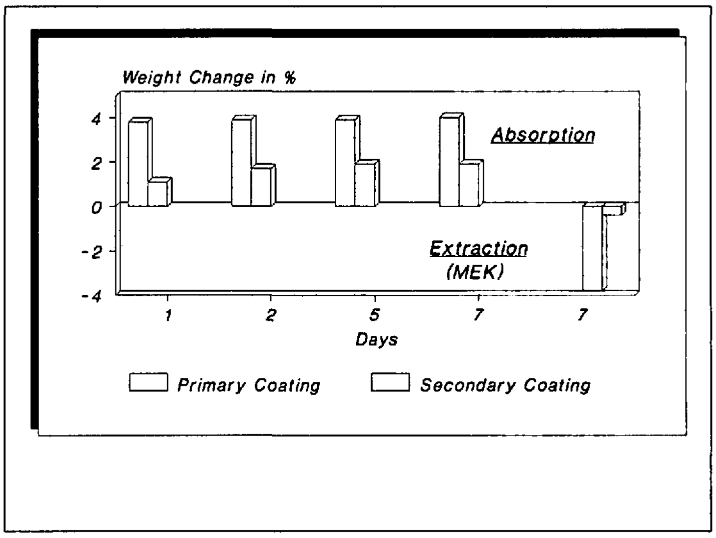


Fig. 7. *Absorption of H_2O and extractables (in ethyl methyl ketone)*

buffer primary coat and a hard top layer (secondary coating).

The primary coating provides a compliant enclosure which decouples the fibre mechanically from its surrounding, the secondary coating acts as a stiffener which preserves the fibre from external forces [2][7]. These functions must be performed over a wide temperature range, preferably from –60 to +80°. Additional the coating must be resistant towards heat and oxygen to maintain its performance and the fibres reliability as long as possible.

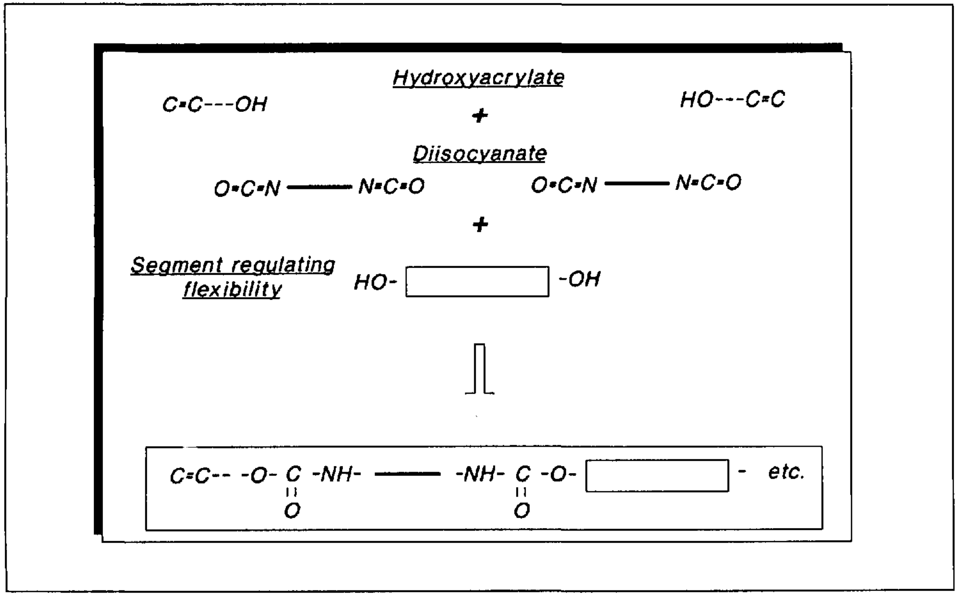
UV-curable acrylates, especially based on polyurethanes, are one preferred class of fibre coatings due to their high curing rate combined with extended 'pot lives' and good rheological properties. The schematic structure of these polyurethan based acrylates is given in *Scheme 5*. The key role plays the segment regulating the flexibility which is often based on linear or branched polyethersegments [8][9]. It is very flexible in formulations used for primary coatings and less flexible but not rigid in formulations used for secondary coatings.

The mentioned different demands for primary and secondary coating are also mirrored in the other ingredients of the coatings: while in the buffer coating reactive monomers are usually used, difunctional monomers are incorporated into the top coating resulting in higher cross-linked networks after curing thus giving the required mechanical resistance (*Fig. 5*).

The different elastical character of the two layers is also presented in *Fig. 6* where the tensile modulus E' is shown in dependance on temperature.

The key demand for the top-coat is to give chemical resistance and to protect the optical fibre to water mirrors itself in the low absorption of water even in long time tests and its resistance to ethyl methyl ketone (*Fig. 7*).

Scheme 5. *Acrylated Polyurethane Resins for Optical Fibre Coatings (schematic)*



4. Remarks

Radcure products have conquered an important segment of the coatings market. Research is focussed on developing new applications. New types of photoinitiators are fragmented into pieces which do not absorb UV-light, making thicker films applicable and already led to a number of pigmented systems.

Outdoor applications of radcure products are rar. This is caused by the curing suppressing properties of light stabilizers which are essential in getting light- and weather-resistant coatings. To overcome this new light stabilizer systems are under investigation, first results are promising.

The above mentioned shrinkage of the radcure coatings during curing leads to adhesion problems especially on metal thus excluding this technology of the big market of metal coating in the past. But even in this difficult application field research led to pilot systems with low shrinkage and promoted in adhesion which may be applicable on metal.

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