ELSEVIER

Polymer 40 (1999) 5297–5302

polymer

Electron-beam curing of thick thermoset composite matrices

T. Glauser, M. Johansson, A. Hult*

Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Received 26 November 1997; received in revised form 19 August 1998; accepted 9 October 1998

Abstract

Electron-beam (EB) curing of two epoxy resins, one acrylated and one methacrylated, has been investigated. The change in thermomechanical properties, such as T_g, and the change of residual unsaturation have been studied as a function of dose. These results, in combination with in situ measurements of the temperature during cure, have shown the importance of sample geometry for the final properties of the thermoset. The thermal history of the sample during cure greatly affects the properties of the cured resin. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Electron beam; Curing; Acrylate

1. Introduction

High energy electron beams (EBs) have found numerous applications since their first use in the 1950s. Applications range from sterilization of medical equipment to curing of coatings or composites [1]. The use of electron beams to initiate polymerization reactions is one area on which much interest has focused. EB curing possesses some special features compared with conventional curing, for example, when curing thick composites, much lower temperatures are reached and the curing process can be better controlled than with thermal curing [2].

Work on electron-beam curing of polymers has been conducted since the 1960s, mainly by Charlesby [3,4] and Chapiro [5]. The specific field of EB curing of thermoset composites has been studied since the 1970s. Saunders and coworkers [6,7] and Singh et al. [8] have been working on EB curing of numerous resins, such as acrylated epoxies. They have not only studied the properties of the EB cured composite, but also investigated the effect of the electron beam on the resin as well as on the fiber and its sizing. Both carbon, glass and aramid fiber reinforcements have been evaluated. Béziers et al. [9] have been working on EB curing of composites since the 1970s and have published papers on the curing of filament wound composites. Their work dealt with epoxy acrylates and bismaleimide resins.

The curing of vinyl monomers such as acrylates, methacrylates and maleimides by means of high energy electron beam irradiation normally proceeds via a free-radical mechanism, where the initiating species are formed by bond cleavage within the resin structure. Numerous other reactions also occur as side reactions to various extents during the polymerization, making the overall system difficult to evaluate. EB curing is sensitive to oxygen inhibition, like other free-radical curing process, such as UV curing. This problem, which is of much importance for the coating industry, is of less importance in the case of thick composites. EB curing can also proceed via a cationic mechanism by using suitable onium salts as initiators. Crivello et al. [10], for example, studied the cationic curing of epoxy resins using onium salts as initiators.

The present study investigates the network formation when EB curing acrylate and methacrylate resins in order to obtain a better understanding of how some of the curing parameters affect the structure build-up. The resins used in this study were selected because they were simple, well-defined and differ only in their reactive groups, so that some conclusions about the effect of resin structure can be drawn.

2. Experimental

2.1. Instrumentation

EB curing was performed with a pulsed sweeping electron beam, which was produced by a microtron accelerator with an energy of 6.5 MeV and a current of 80 mA. The dose could be varied between 1 and 3 Mrad per sweep by changing the length of the pulse. The dose calibration of the

---

* Corresponding author.

PII: S0032-3861(98)00752-6

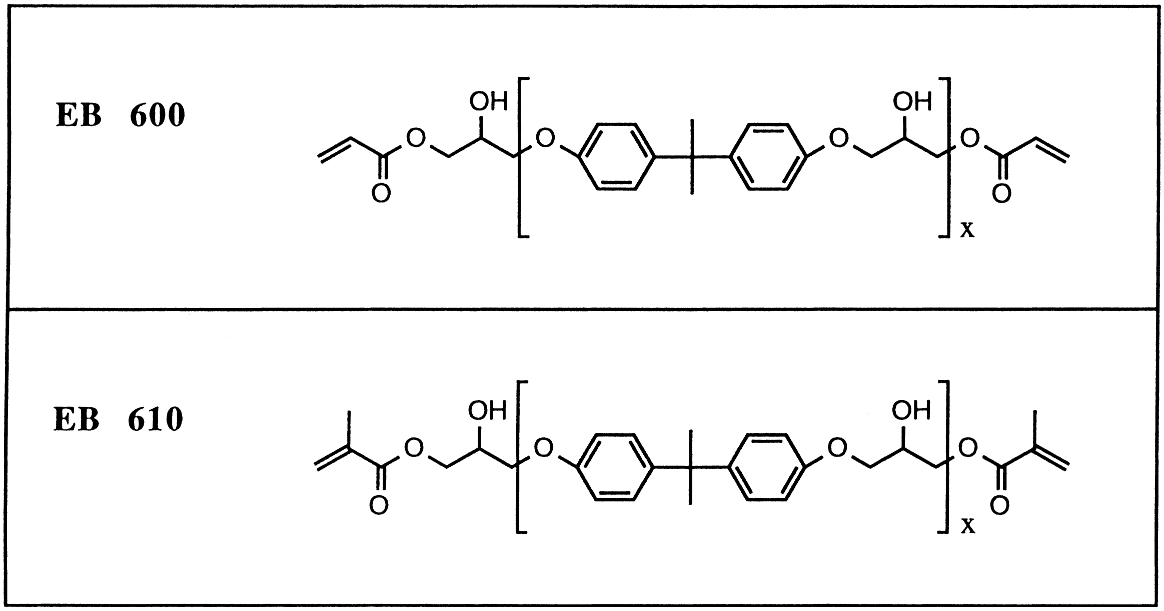

Fig. 1. Structure of the two monomers based on epoxy bisphenol-A. They are distinct by their reactive groups, EB600 being an acrylate, whereas EB610 is a methacrylate. SEC runs give $x = 1$–2 and low polydispersity for both monomers.

instrument was performed with a Risø calorimeter. The temperature of the resin during cure was measured with a thread thermocouple and recorded by a Combilab equipment from Chipzobits Digitalteknik AB. The thermomechanical properties were measured with a Dynamic Mechanical Thermal Analyzer (DMTA) Mk II from Polymer Laboratories. The FT-Raman spectra were measured with a FT-Raman Spectrometer 1700X from Perkin Elmer. The UV spectra were recorded with a Diode Array Spectrophotometer HP 8451A from Hewlett Packard. The SEC runs were performed at room temperature on a Waters 6000A pump equipped with two PL gel 10 μm mixed-B columns (300×7.5 mm^2) from Polymer Labs and a refractive index detector. Chloroform was used as mobile phase using a flow rate of 1 ml/min. Calibration was performed with linear polystyrene standards in the molecular weight range 2000–3×10^6 g/mol.

2.2. Materials

Two resins from UCB, Belgium, based on a bisphenol-A-epoxide, were investigated. One was acrylate functionalized (Ebecryl 600, or EB600), whereas the other one had methacrylate reactive groups (Ebecryl 610, or EB610). Their structure can be seen in Fig. 1. SEC runs show a low polydispersity and similar values for both resins (EB600: $M_n =$ 700 Da, $M_w = 790$ Da, PDI = 1.13; EB610: $M_n = 710$ Da, $M_w = 780$ Da, PDI = 1.10). No initiator was used. The release agent (Water-release), used when curing in an aluminum mold, was supplied by Zywax Inc.

2.3. Methods

Two types of samples were made, one with a thick and one with a thin geometry, as described in Fig. 2. The thick samples were cured in 10 ml glass vials (Ø 2 cm). Test specimens ($2 \times 2 \times 40$ mm^3) were cut out of the center of the cured cylinder. Thin samples were polymerized as plaques ($100 \times 100 \times 2$ mm^3) and cured in a 10 mm thick aluminum mold. A Mylar film covered the sample to avoid oxygen inhibition at the surface. Test specimens ($2 \times 2 \times$ 40 mm^3) were cut out of the plaque. Samples were cured

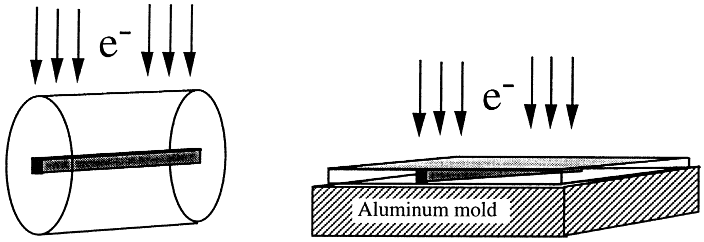

Fig. 2. Sketches of the two types of molds used in this study. The test samples ($2 \times 2 \times 40$ mm^3) are represented by the dark gray rods. Samples cured in a glass vial (Ø 20 mm) and cut out of the center of this cylinder are named 'thick' samples. The 'thin' samples are cut out of a plaque ($2 \times 100 \times 100$ mm^3) and have one face in contact with the aluminum mold (10 mm thick) during cure. The opposite side is covered by a Mylar film in order to prevent oxygen inhibition.

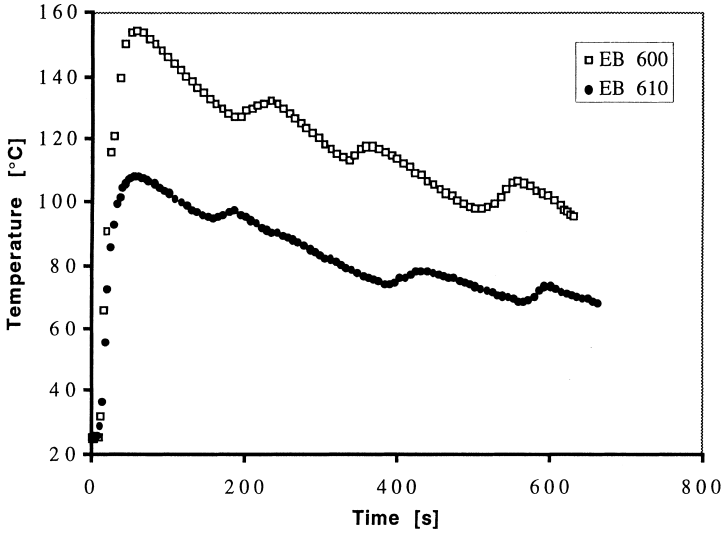

Fig. 3. Thermogram of EB600 and EB610, cured with 4 × 2.5 Mrad. The strongest exotherm occurs during the first sweep. The following irradiations only give small temperature increases, mainly due to the slowing down of the electrons by the resin.

with one, two, three or four sweeps of 2.5 Mrad each, where the dose of 10 Mrad was considered to be sufficient for a complete cure. The received dose was measured by cellulose triacetate (CTA) films placed on top of each sample. The change in absorbance of the film at 280 cm^{-1} was measured with a UV spectrometer. The storage modulus (E'), the loss modulus (E''), and tan δ were measured versus temperature by DMTA with a double cantilever geometry at a frequency of 1 Hz and a heating rate of 2°C/min. The glass transition temperature (T_g) was defined as the peak of the tan δ curve. The residual unsaturation was measured by FT-Raman spectroscopy by monitoring the unsaturation peak at 1635 cm^{-1}. The peak of the aromatic rings at 1609 cm^{-1} was used as an internal reference. A peak deconvolution was performed, minimizing the quadratic error between the measured spectra and the sum of three peaks given by the Lorentz formula.

3. Results and discussion

Both monomers used in this study undergo a free-radical polymerization when subjected to an electron beam. The two resins differ only in the structure of their reactive groups, one acrylate and one methacrylate (cf. Fig. 1). Since it is likely that the initial scission of a bond, which will give an initiating species, occurs in the vicinity of the carbonyl group, it can be speculated that these resins will have similar initiation mechanisms. The main differences between the resins is their difference in reactivity and, at later stages of the reaction, their difference in mobility of the monomer in the partly crosslinked system. Comparing the polymerization of methylacrylate with methylmethacrylate monomers, it has been shown that both heat of polymerization and propagation rate are substantially larger for the former [11]. Transferred to the system studied in our case, this means that the acrylate functional resin may produce more heat and polymerize more rapidly. For a crosslinking system, vitrification will/may occur at some stage during the reaction and thus become an additional factor to take into account in the network formation. This factor is related to the physical state of the system, i.e. temperature and T_g of the network. Polymethacrylates generally exhibit a higher T_g compared with polyacrylates due to a stiffer main chain [12], which will be of importance if the polymerization proceeds into the vitrified state. Another difference between polyacrylates and polymethacrylates when they are subjected to high energy irradiation is that chain scission dominates over chain coupling for polymethacrylates while the opposite holds for polyacrylates [13]. The amount of chain scissions/couplings is, however, small compared with the addition reactions in the polymerization process.

3.1. Temperature evolution

It is often said that EB curing proceeds at ambient temperature. However, this is not entirely true since heat evolves from the curing reaction as can be seen in Fig. 3. The heat formation during the cure is mainly governed by the enthalpy of polymerization and the heat dissipation to the environment or the mold. The exotherm due to the polymerization occurs mainly during the first sweep of the electron beam [14]. Each new sweep gives rise to a small exotherm which is mainly due to the slowing down of the incoming electrons. This can be shown by subtracting the curve shown in Fig. 3 with the thermogram obtained when simultaneously re-irradiating a fully cured sample. The 'reboosting' of the free-radical polymerization by the subsequent sweeps does not give an exotherm large enough to be detected by the thermocouple.

Table 1
Highest temperature during cure (T_{max}), glass transition temperature and residual unsaturation (res. unsat.) for both thick and thin samples cured with different doses. * For thin samples T_{max} variation is large, but in all cases lower than with thick samples

	Acrylate			Methacrylate		
Dose (Mrad)	T_{max} (°C)	T_g (°C)	Res. unsat. (%)	T_{max} (°C)	T_g (°C)	Res. unsat. (%)
Thick samples						
2.5	150	150	13	110	156	25
5	150	158	11	110	169	18
7.5	150	159	8	110	173	16
10	150	159	7	110	177	15
Thin samples						
2.5	*	81	13	*	117	25
2.5 re-run	—	—	—	—	123	—
5	*	104	11	*	130	18
7.5	*	108	8	*	136	16
10	*	117	7	*	141	15

The geometry of the sample and the mold is of great importance since it affects the heat dissipation rate from the specimen. The maximum temperature reached during the cure varies with the geometry, as can be seen in Table 1.

A thin sample will be cooled much faster, thus decreasing the propagation rate of the polymerization and reducing the mobility of the reactive species in the vitrified system, hence slowing down the overall curing rate. The thin sample in this study is cured in an aluminum mold, which by its high heat conductivity increases the heat dissipation rate compared with a thick sample. The aluminum mold produces some heat by slowing down incoming electrons, but this effect is negligible compared with the exotherm of the polymerization. These results transferred to the case of composites indicate that the fiber content is an important parameter because the heat production per cubic centimeter is reduced. The heat dissipation by the fiber leads to extra cooling, especially when using a fairly good thermal conductor such as carbon fibers. Since the first sweep gives, by far, the highest temperature rise, it can be considered to dominate, if a high dose rate is used, the thermal history of the newly cured samples. The structure of the monomers will also affect the thermal history of the system by intrinsic differences in reactivity between the monomers. When comparing the different resin systems in the current study, higher heat of polymerization and propagation rates of the acrylate resin will result in higher temperatures than the more slowly reacting methacrylate resin [12].

3.2. Network formation

For the acrylate a steady decrease of residual unsaturation can be seen, as shown in Table 1. Once the material approaches the ‘fully cured’ state, the residual unsaturation

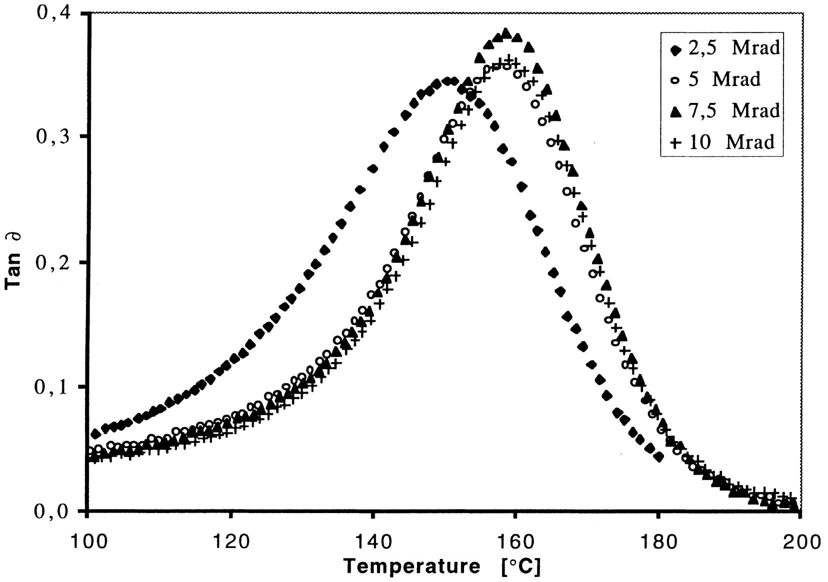

Fig. 4. For the acrylate resin the tan δ peaks are shifted to a higher temperature with increasing dose. Between 5 and 10 Mrad the change is only marginal.

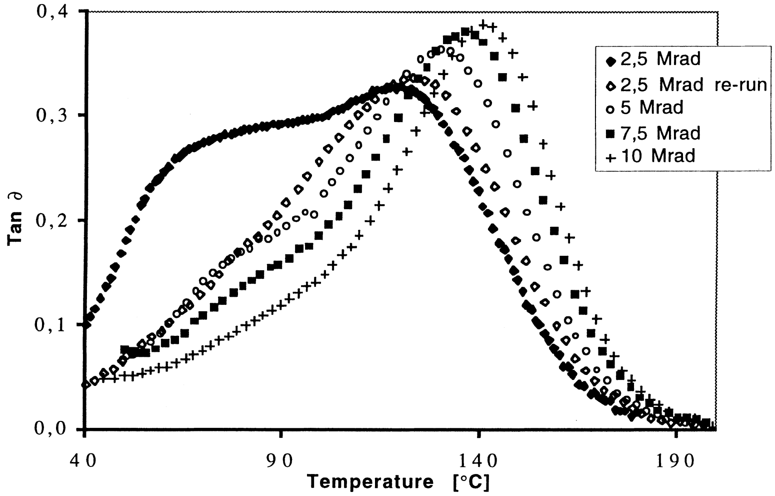

Fig. 5. Tan δ peaks for thin samples of EB610 cured with increasing doses. When using low doses a bump due to trapped reactive species can be noticed. This effect disappears when reheating the sample.

levels out since the reduced mobility of the remaining reactive groups restricts further reactions. The methacrylate follows the same kind of trend, though leveling off at a higher value since the monomer has a lower mobility in the formed network, i.e. the crosslinking of the methacrylate continues into the vitrified state.

Fig. 4 shows a shift of the tan δ peak for the acrylate as a function of dose, to higher values with increasing dose. The propagation of the crosslinking reaction leads to the formation of a tight and rigid network. The T_g of the material increases at the investigated doses up to a maximum value where it levels out.

The methacrylate shows the same trend but reaches a higher T_g, as expected considering the more rigid backbone structure. It is worth noticing that in this case the ultimate T_g is much higher than the highest temperature reached during the cure (T_{max}). On the contrary, the curing of the acrylate resin occurs at temperatures above the final T_g of the cured network, hence in a less rigid environment. This difference in the temperature profile during the crosslinking process is one reason for the higher level of residual unsaturation in the case of the methacrylate resin.

The higher amount of residual unsaturation in the methacrylate resin also indicates a lower crosslink density of the network since the only difference between the monomers is the type of reactive group and not the size or the functionality. The higher T_g of the methacrylate network can be attributed to a higher chain stiffness induced by the methyl group. The fact that for the methacrylate resin $T_g \gg T_{max}$ shows that molecular diffusion plays a smaller role in EB curing than in thermal curing, where the reaction rate rapidly slows down when T_g of a crosslinking resin reaches the temperature of cure. On the other hand, the larger amount of residual unsaturation when $T_g > T_{max}$ (methacrylate) compared with when $T_g < T_{max}$ (acrylate) indicates that, although the effect of diffusion is reduced, it still affects the final properties of the material.

3.3. Vitrification

When making thin acrylate samples, lower values of T_g are reached (cf. Table 1). Since these samples were subjected to lower temperatures during cure, the mobility of the monomer was reduced. It can be seen that the residual unsaturation is higher, and subsequently the lower T_g can be attributed to a lower crosslink density. When testing thin samples of the methacrylate resin, a ‘bump’ can be seen on the tan δ curve of the sample subjected to a dose of 2.5 Mrad, as can be seen in Fig. 5. When performing a temperature scan on this partially cured material in the DMTA, the trapped radicals and the unreacted methacrylate groups acquire enough mobility to meet each other, inducing further crosslinking. This post-curing resulted in an increase in T_g while testing the material.

A second DMTA run (cf. Fig. 3, 2.5 Mrad re-run) conducted on the same material shows that the bump has disappeared and that the T_g has increased. The vitrification point of the curing system occurs at an earlier stage of the reaction in the case of the thin geometry due to lower temperatures in the samples. This leads to a larger fraction of unreacted double bonds in the system compared with the thick samples. When the cured sample is heated above its T_g for a sufficient time, unreacted double bonds will react with one another, decreasing the residual unsaturation and increasing the mechanical properties. This effect is not seen to the same extent on ‘fully cured’ samples, since the crosslinking is forced to occur in the vitrified state. Vitrification occurs early in all samples, but is not seen as clearly as in the sample discussed above. The re-run shows that there are reactive species trapped in the vitrified network of a partially cured resin, and that they are able to initiate crosslinking when ‘devitrified’. Comparing fully cured samples with a thick and a thin geometry, it is seen that an early vitrification will reduce the final T_g and increase the residual unsaturation.

4. Conclusions

EB curing of the acrylates and methacrylates used in this study is a free-radical polymerization process. For both resins, the T_g increases with increasing dose up to a plateau level, after which no significant increase of T_g can be noticed when further increasing the dose. The monomers differ by their reactivity and their mobility in the crosslinking network. The more reactive acrylate exhibits a faster and a stronger heat production than the methacrylate, inducing a higher maximum temperature during the polymerization. The methacrylates have a higher amount of residual unsaturation due to a lower mobility of the monomer in the crosslinking network. Nevertheless, the cured system shows a higher T_g due to a stiffer backbone chain. The thermal history of the sample is important for the final properties of the thermosets. This was demonstrated by comparing resins cured as thick samples in bulk, where high temperature was reached, with thin samples cured in a thick aluminum mold which dissipates the thermal energy generated during the cure. In the latter case the mobility of the monomers is reduced, and consequently the reaction rate is lowered. Therefore, the reaction is terminated before a full cure is reached. By doing a thermal post-cure of a partly cured resin, the T_g is increased to a value between the initial T_g and the T_g of the fully cured resin. This indicates the presence of active species in the vitrified network, which can induce further polymerization when devitrified by a temperature raise. To summarize, the effect of thermal history on the matrix properties is of importance when designing an EB cured composite part. The thermal history will be affected by several factors such as specimen geometry, mold material, and amount and type of fiber.

Acknowledgements

The Council of the European Community (CEC) is gratefully thanked for sponsoring this study via a Brite-Euram project, BE 951449-Technicopolis. UCB is acknowledged for supplying us with resins. Aerospatiale, and the other Technicopolis members, are thanked for their support and constructive debates. Professor T. Reitberger is thanked for many valuable discussions.

References

[1] Spinks JWT, Woods RJ. An introduction to radiation chemistry, 3rd ed. New York: Wiley, 1990.
[2] Vendroux G, Hocquellet M, Boursereau F, Dourthe P. RadTech Europe 97, Conference Proceedings, 1997:462.
[3] Charlesby A. Atomic radiation on polymers. Oxford: Pergamon Press, 1960.
[4] Charlesby A. Rad Phys Chem 1991;37(1):5.
[5] Chapiro A. Radiation chemistry of polymeric systems. New York: Interscience, 1962.
[6] Saunders CB, Lopata VJ, Kremers W, Chung M, Singh A, Kerluke DR. Rad Phys Chem 1995;46(4–6):991.
[7] Saunders CB, Singh A, Lopata VJ, Kremers W, Tateishi M. ACS Symp Ser 1993;527:305.
[8] Singh A, Saunders CB, Barnard JW, Lopata VJ, Kremers W, McDougall TE, Chung M, Tateishi M. Rad Phys Chem 1996;48(2):153.
[9] Béziers D, Perilleux P, Grenie Y. Rad Phys Chem 1996;48(2):171.
[10] Crivello JV, Walton TC, Malik R. Chem Mater 1997;9:1273.
[11] Brandrup J, Immergut EH. Polymer handbook, 3rd ed. New York: Wiley, 1989.
[12] van Krevelen DW. Properties of polymers, 3rd ed. London: Elsevier, 1990.
[13] McGinnis VD. In: Kroschwitz JI, editor. Encyclopedia of polymer science and engineering, vol. 4. New York: Wiley, 1986.
[14] Patacz C et al. FTIR monitoring of the EB initiated polymerization of some acrylate compositions. In: RadTech Europe 97, 8th Conf. on Radiation Curing, 17–18 June 1997.