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Radiation Physics and Chemistry 63 (2002) 481–483

Radiation Physics and Chemistry

www.elsevier.com/locate/radphyschem

Characterization of a clear coating cured by UV/EB radiation

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Abstract

The quality and performance of the polymeric materials cured by ultraviolet (UV)/electron beam (EB) radiation depends on the components of coating formulation, as well as the type of radiation used in the curing process. The aim of this study was to establish the correlation between the cure degree of a clear coating irradiated with different radiation doses of UV or EB and the tensile properties of the polymeric films obtained. The cure degree was measured by DSC and FTIR.

Keywords: Radiation curing; Photocurable coatings; UV/EB cured polymers

1. Introduction

The materials curable by ultraviolet (UV) or electron beam (EB) such as inks, varnishes, adhesives and coatings are reactive compounds made by oligomers, monomers, photoinitiators, pigments and additives (Pappas, 1980). Under irradiation these substances polymerize and cross-link producing thermoset films. The physical and tensile properties of the polymeric films obtained are largely dependable on coating formulation and also on the type of radiation used. The aim of this work was to correlate the following parameters: (a) the cure degree reached by the cured films, (b) the type of radiation used, and (c) the radiation doses in both curing processes. Tensile property determinations were used, to evaluate the mechanical performance of the cured coatings as a function of cure degree induced by UV or EB.

2. Experimental

2.1. Samples preparation procedure

The clear coating consists of an aliphatic urethane diacrylate oligomer (Ebecryl 270), 1,6 hexanediol diacrylate monomer (HDODA), both supplied by UCB do Brasil Ltda., and the photoinitiator 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173) supplied by Ciba Especialidades Químicas Ltda. The liquid coating was put down in layers, 50 μm thick, on glass substrates using an appropriate extensor and then cured by UV or EB radiation. The UV curing process was carried out at room temperature using equipment named Labcura, from Germetec Ultraviolet & Infrared Technology Ltda., with a medium pressure mercury lamp and a belt with variable speed. The ultraviolet radiation doses were in the range of 50–1200 mJ/cm^2, which were measured by an IL 390B Light Bug radiometer from International Light Inc. Other samples with the same composition but without photoinitiator were cured by EB, under N_2 atmosphere, with doses in the range from 1–30 kGy using the Dynamitron electron beam accelerator with energy of 1.5 MeV.

2.2. Evaluation methods

Cured films were removed from their glass substrates and after that were characterized by fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) to evaluate the cure degree of each sample. The curing qualitative evaluation was made from the attenuation of the FTIR characteristic absorption bands (Roeges, 1995) which was carried out with a Nicolet 360 spectrophotometer. Measurements

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0969-806X/02/$ - see front matter
PII: S0969-806X(01)00592-8

of the reaction heat were performed using a Shimadzu DSC 50, at a heating rate of 10°C/min from room temperature to 250°C. The total amount of heat used in the thermal polymerization reaction can be related to the exothermic peak areas of the DSC curves (Turi, 1981). The cure degrees were calculated based on the value of residual heat from thermal polymerization of samples cured by radiation. The reference heat value for the complete cured sample was considered as the heat of the thermal polymerization of the uncured coating formulation. Tensile mechanical determinations were performed with an universal test machine Instron 5567, according to ASTM D 638-77a standard method.

3. Results and discussion

3.1. FTIR evaluations

The curing process was evaluated by the FTIR attenuation bands. Three absorption bands were considered at the respective wavenumbers: (a) 810 cm^{-1}, which is related to the C–H out of plane deformation mode of the acrylate double bond; (b) 1410 cm^{-1}, related to C–C bond between C = C and C = O acrylate groups, and (c) a doublet at about 1640 cm^{-1}, related to C = C acrylate stretch mode. The spectra of the cured samples showed the attenuation of these bands with the increase of radiation doses. Furthermore, at higher doses these characteristic absorption bands were so weak that measurements of peak area or peak high could not be done.

3.2. DSC evaluations

In Table 1 are given the experimental data obtained from the DSC measurements.

3.3. Mechanical properties

The tensile strength behaviors of the cured samples, as a function of radiation dose, are given in Figs. 1 and 2.

In Fig. 1 it was observed that the values of the stress at break increase up to around 20 kGy and tend to decrease at higher doses. The elongation at break values have shown a noticeable increase up to around 5 kGy and afterwards, a continuous decrease of these values were observed at higher doses. This mechanical behavior could be due to the fact that at doses smaller than 5 kGy the amount of cross-linking in the irradiated material was not able to withstand the applied mechanical load. The decrease tendency of the values of tensile strength and elongation at break, for radiation dose beyond 20 kGy, could be related to some degree of the polymer degradation.

Table 1
DSC experimental results

Dose (kGy)	Reaction heat[a] (J/g)	Cure degree (%)
EB samples		
0	226.4	0
1.6	34.5	84.8
2.6	27.4	87.9
5.2	18.3	91.9
10.4	14.5	93.6
20.8	10.2	95.5
30.2	9.1	96.0
Dose (mJ/cm^2)	Reaction heat[a] (J/g)	Cure degree (%)
UV samples		
0	271.2	0
50	31.1	88.5
100	23.8	91.2
200	19.6	92.8
400	16.3	94.0
600	16.2	94.8
1200	12.4	95.4

[a] Heat from residual thermal polymerization of UV/EB cured films related to sample weight.

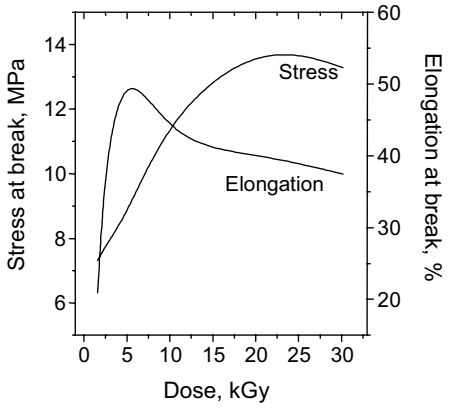

Fig. 1. Tensile strength and elongation at break as a function of EB-radiation dose.

In Fig. 2 it was observed that an increase of the stress at break values for UV cured samples with an increase in the doses up to about 600 mJ/cm^2. Thereafter, the curve showed a stabilization tendency of this measured property. The elongation at break values has shown a decrease in the range of 50–200 mJ/cm^2. After that, a stabilization tendency was observed.

The samples cured with higher doses of EB or UV radiation have shown different tensile strength behaviors, which could be attributed to the different reaction mechanisms, as a consequence that UV is an electro-

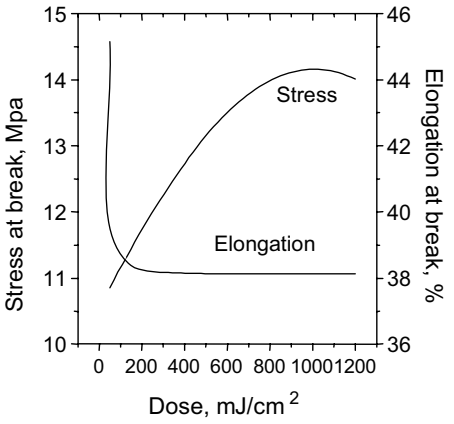

Fig. 2. Tensile strength and elongation at break as a function of UV-radiation dose.

magnetic radiation and EB is an energetic current of charged particles.

4. Conclusion

The cure degree values, evaluated from DSC results, allowed relating the UV and EB radiation doses with the cure degrees of the polymeric films. The samples cured by UV or EB radiation in the dose range of 100–1200 mJ/cm^2 and of 5–20 kGy, respectively, reached equivalent cure degrees.

DSC results have shown that the samples were undercured, even when irradiated at higher doses. The polymer conversion induced by radiation was incomplete, due to reactive species immobilization inside the molecular network. This behavior was also verified by stress at break measurements, which at high doses a stabilization tendency of this mechanical property was observed.

With the evaluation of thermal and mechanical properties of the cured samples it was possible to correlate the effects of UV and EB radiation. The experimental results have shown that EB polymeric films cured up to 20 kGy have more mechanical strength than the UV cured samples with equivalent cure degree.

The EB curing process has the advantage of producing a more depth uniform polymeric film. The main disadvantage of this process is the high cost of the irradiation system, its maintenance and operation. The development of low-cost EB-accelerators with simple operation and maintenance will be necessary conditions to favor the use of this technology in the ink, varnish, adhesive and coating industry.

Acknowledgements

Conselho Nacional de Pesquisa e Desenvolvimento—CNPq, Ciba Especialidades Químicas Ltda., and UCB do Brasil Ltda. are greatly acknowledged.

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