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ACCOMPANYING OF ELECTRON BEAM CURING OF PRINT INKS FOR PLASTIC PACKAGES

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ABSTRACT

By the popularization of inks on the market, some problems arose due to the volatile organic compounds (VOCs) that are liberated to the atmosphere when the solvents are allowed to evaporate. So, the recent demand for more environmentally friendly restricts the emission of VOCs. In this context, the solution found by paint manufacturers to meet these requirements is the replacement of solvent-based paint systems for systems such as powder paint, water-based inks, high solids content, or cured by UV/EB radiation (ultraviolet light/electron beam). In the latter, the solid film formation occurs through chemical reactions induced by incident radiation, between the resin and monomers, without the emissions of volatile pollutants in the air. So, this study aims to establish the correlation between the degree of cure of pigmented films and different doses of EB in order to analyze the importance of controlling the degree of cure of polymeric films of paints. It's known that a sub-cured film ink is partially soluble and presents low chemical and mechanical resistance whereas an over-cured film ink is very rigid and brittle. Thus, determining the degree of cure is of great importance in the quality of the polymer film formed. Tests were performed with films of basic color inks for printing / decoration of plastic packaging, using thermal analysis techniques for samples at different doses of radiation used in the induction of curing reactions.

1. INTRODUCTION

During the last decades, some alternative technologies have been come up in order to reduce environmental impacts caused by widespread consumption of short lifetime products. As punctuated by Clark [1], electron-beam (EB) ink curing can properly fit this category because of some convenient common characteristics: sustainability, flexible manufacturing, energy efficiency, increased return of investment (ROI), higher quality products, lower greenhouse gas and volatile organic compounds (VOC) emission. Additionally, the two processes can be used for the same or similar applications, such as printing, coatings and adhesives that means where only thin layers are being processed. However, for thicker layers, films, and sheets, even opaque and highly filled, as well as composite materials, electron beam radiation is the method of choice [2].

To put it briefly, radiation curing technology is defined as the formation of solid ink film through chemical reactions induced by incident radiation, i.e. EB [1]. The reactive species produced by electron beam are dispersed randomly throughout the entire thickness of the material (Fig. 1b). The penetration depths as well as the amount of energy deposited can be regulated with a great deal of accuracy [2]. In other words, EB electrons have ability to penetrate through the matter in order to induce free-radical formation, because they contain greater amount of energy than chemical bond does [1,4].

Takahashi and collaborators [4] pointed out that EB radiation can easily cure the monomer, which compounds the colorants such as carbon, titanium, leads and zinc, although the exposure to another radiation sources can hardly do.

Radiation-curable coatings for flexible substrate are mostly reactive formulations where the organic solvents (VOC) are replaced by reactive diluents such as monomers. Since they are usually highly viscous, they tend to produce rough surface, so it is crucial to define some curing parameters, as described by some authors [2,5]:

- Coat weight (layer thickness);
- Application method;
- Coat viscosity and viscoelasticity;
- Coat weight accuracy required;
- Coating speed;
- Substrate to be cured.

The usage of EB curing for coatings on flexible substrates is increasing nowadays [2]. They have a considerably high production rate (100 m min^{-1} to 300 m min^{-1}), therefore lower energy electrons and moderate to high power beams are sufficient. The following EB cure applications in printing and graphic arts are reported by Drobny [2]:

- High gloss cosmetic and cigarette packaging;
- Greeting cards;
- Aseptic packaging;
- Record album jackets;
- Stamps;
- Banknotes.

As described by Salleh and collaborators [3], many research papers are dedicated to utilize in a lesser extent EB curing techniques. So, this paper aims to evaluate the degree of cure of pigmented films at different EB radiation doses in order to analyze the importance of controlling the degree of cure of polymeric films of paints.

2. EXPERIMENTAL

2.1. Materials

The following materials were applied for the preparation of the EB-curable compositions:

- Bisphenol A epoxy diacrylate (EBECRYL® 3720-TP25, Cytec Industries Inc.) diluted 25% by weight with tripropylene glycol diacrylate (TRPGDA, Cytec Industries Inc.);
- Trimethylolpropane triacrylate (TMPTA, Cytec Industries Inc.);
- Talc (Nicron® 674, Luzenac America, Inc.);
- Polydimethylsiloxane (Pure Silicone Fluid 100,000cSt, Clearco Products Co., Inc.);

- Quinone derivative in propoxylated glycerol tri-acrylate (Irgastab® UV 22, Ciba Specialty Chemicals Inc.);
- Polyethylene/Polytetrafluoroethylene wax (CeraSPERSE® 164, Shamrock Technology, Inc.);
- Carbon black (Printex® 45 powder, Evonik Degussa GmbH)
- Yellow pigment derived from diarylide m-xylidide (Irgalite® Yellow LBIW, Ciba Specialty Chemicals Inc.)
- Blue pigment derived from phtalocyanine (Hostaperm Azul B2G 01-BR, Clariant Pigmentos e Aditivos Ltda.);
- Ruby pigment derived from monoazo (Rubide 4B, Hongyan Pigment Chemical Co., Ltd.);
- Titanium dioxide.

2.2. Methods

2.2.1. EB irradiation process

A manual applicator type Quick-Peek (Boanitec Indústria e Comércio Ltda., Cotia, SP, Brazil) was used to apply the EB-curable formulation over a poly(vinyl chloride) substrate. The thickness of the coating film was 7.0 µm ± 1.3 µm.

For the EB curing process, the formulations were coated in aluminum crucibles and subjected to electron beam irradiation the Dynamitron electron beam accelerator with energy of 1.5 MeV, under N_2 atmosphere to avoid the competition of oxygen and the monomer in reacting with radicals, that would lead to a non-uniform distribution of these radical and a slower reaction rate [6,7]. The doses provided by the machine were 1, 4, 10, 15, 20 and 30 kGy for double pass by the electron beam.

2.2.3. Evaluation methods

Measurements of the reaction heat were performed using a Shimadzu DSC 50, sealed aluminum crucible at a heating rate of 10°C min^{-1} from room temperature to 350°C under N_2 atmosphere at flow rate of 50 mL min^{-1}. The total amount of heat used in the thermal polymerization reaction can be related to the exothermic peak areas of the DSC curves [8]. The reference heat value for the complete cured sample was considered as the heat of the thermal polymerization of the uncured coating formulation. In order to evaluate mass loss, crucibles containing the print inks have been weighted before and after DSC runs.

Thermal stability of the samples was accompanied using a Shimadzu TGA 50, platinum crucible at a heating rate of 10°C min^{-1} from room temperature to 800°C under air at flow rate of 50 mL min^{-1}.

3. RESULTS AND DISCUSSION

Fig. 1 to 5 present the DSC curves for black, white, blue, yellow and red print inks, respectively, pre- and post-EB cured at different radiation doses, and TG curve for uncured compositions.

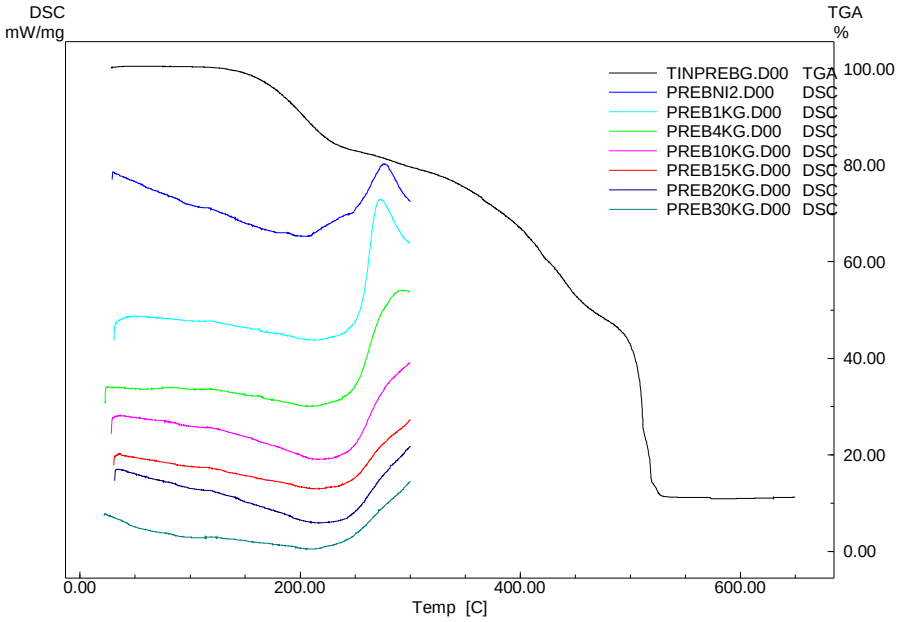

Figure 1. DSC curves for black print ink pre- and post-EB cured.

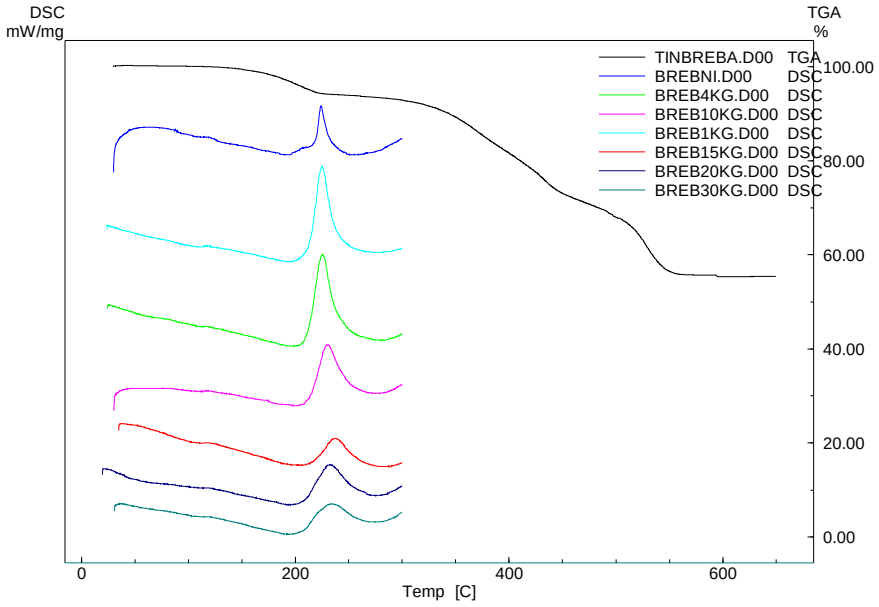

Figure 2. DSC curves for white print ink pre- and post-EB cured.

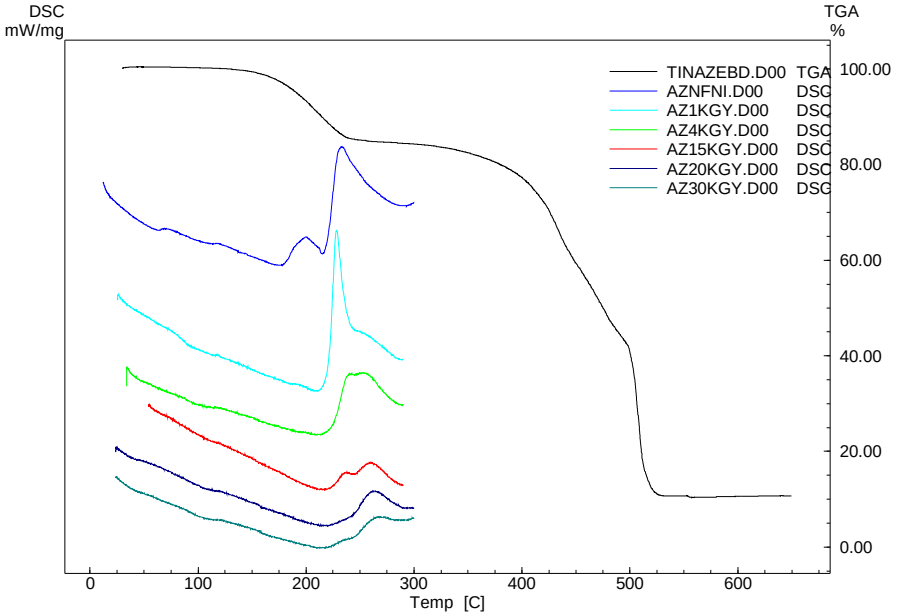

Figure 3. DSC curves for blue print ink pre- and post-EB cured.

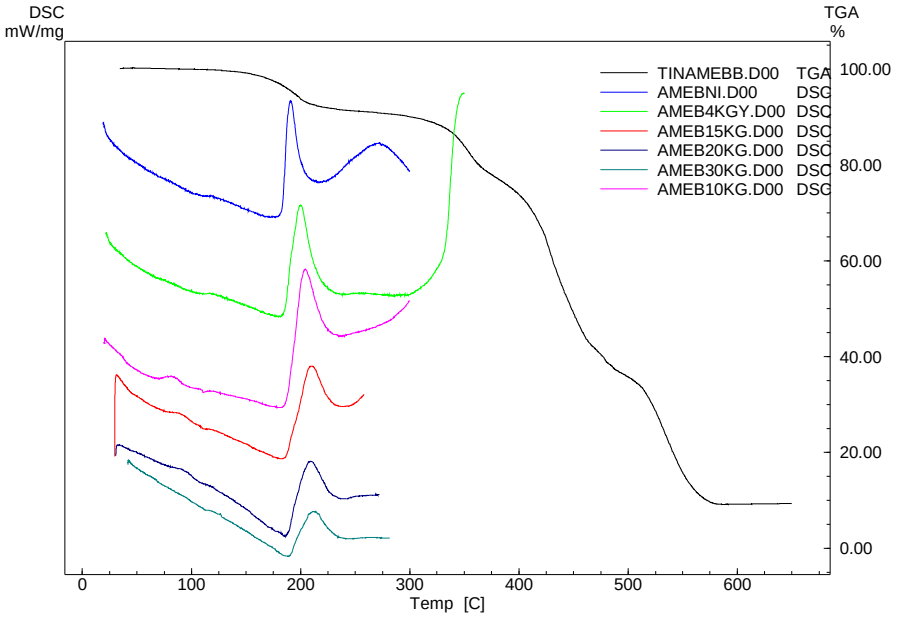

Figure 4. DSC curves for yellow print ink pre- and post-EB cured.

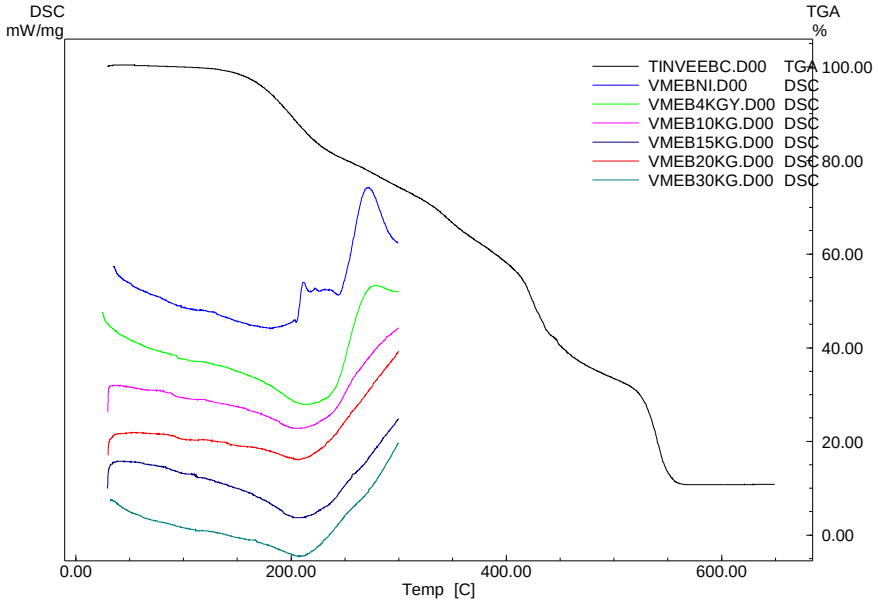

Figure 5. DSC curves for red print ink pre- and post-EB cured.

As it can be seen by the TG curves, all formulations present the same thermal behavior under high temperatures, except the white print ink due to its higher content of inorganic pigment (mass loss is about 45%). The first step of mass loss (from 180ºC to 220ºC) can be attributed to the volatilization of parts of some components, mainly monomers.

When the thermal energy is enough to induce polymerization reactions, a higher amount of energy is instantly liberated once the polymerization is an exothermic event. A tri-dimensional polymeric network is then formed by cross-linking. On the other hand, the temperature rises quickly and part of the non-reacted components is volatilized, which is an endothermic phenomenon.

So, by analyzing Fig. 1 to 5, initial mass loss comes to affect directly DSC analysis. It is impossible to calculate the consumed energy during volatilization. It is known that the resulting energy balance of both events – curing and mass loss – is exothermic. On thermally-curable formulations, the curing degree can be estimated, by DSC measurements, calculating the enthalpy of the exothermal peak corresponding to the curing reaction [7]. However, the studied print inks are not formulated for thermal curing, but for EB induced reaction, that occurs at room temperature.

It could be observed that even samples cured at low doses (1 to 10 kGy) have not presented meaningfully mass loss during the heating process. That means that non-reacted species have been trapped in the polymeric cross-linked structure. By this way, it is not possible to evaluate the curing degree induced by different radiation doses using the relation between uncured and residual enthalpy of reactions determined by DSC.

Besides, some components, such as ruby pigment, have a particular behavior of thermal degradation that can interfere on the measurement of reactions enthalpy, as it can be observed at Fig. 5.

4. CONCLUSIONS

DSC technique is not adequate to quantify curing degree of radiation-curable formulations, but trustable results could be obtained by using either hermetically sealed crucibles that resist internal pressures higher than 300 kPa or pressured DSC cells.

The obtained results allow observing that even the higher studied dose (30 kGy) do not promote a resulting 100% curing degree. It's acceptable a residual uncured fraction around 10%, which reside trapped in the tri-dimensional network.

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