Study of Accelerated Degradation of Pigmented UV-Cured Print Inks

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Abstract

Print inks have assumed an important role on finished materials, such as plastic packages, which can have a long lifetime when disposed as municipal waste. By this way, it is important to evaluate the influence of physical parameters on the degradation of shot lifetime substrates covered by pigmented print inks cured by UV radiation.
Keywords: UV technology; pigmented print inks; thermal degradation; oxidation

Introduction

The contemporaneous society has paid special attention to packages constituted of plastic materials. By this way, manufacturers are examining processes which are environmentally friendly, cost effective, and energy efficient. As mentioned by some authors [1-4], one such technology that has become more popular and more economically feasible around the world is ultraviolet (UV) and electron beam (EB) curing technology. In this technology, conversion of liquid compositions to solid films is designed to occur when radiation interacts with matter, where either high-energy electron penetrates or photons cause only surface effects. Consequently, this will lead to formation of a polymeric network with high molecular weight.

Sallet et al. [3] say that EB cured coatings are usually uniformly cured due to the full-depth penetration of the accelerated electrons. This renders the EB cured coatings to be hard but brittle. Meanwhile, its UV counterparts tend to be less "cured" due to the photoinitiators which absorb more of the UV radiation being at the surface, resulting in the surface having the highest radical concentration. By this way, both techniques are indicated for curing varnishes, inks, adhesives and coatings.

Another important factor described by Yakahashi et al. [5] is that UV radiation needs the incorporation of photoinitiators which are then capable to induce polymerization. As reported by Bardi & Machado [6], a higher degree of curing to take place as a result of enhanced molecular mobility, resulting in a more homogeneous crosslinked network, as well as decreased material cure shrinkage after gelation, and improved substrate adhesion due to lower stress inside the cured film. Additionally, UV equipments are more accessible and less costly than EB ones, which is a leading factor on industry and market nowadays.

Although it is widely known that radiation curing do not emit volatile organic compounds (VOC), once compositions are solvent-less [2,4,7,8], the high degree of crosslinking of the cured films makes the products to last longer when discharged at the environment, sometimes even increasing the

lifetime of plastic substrates[9]. By this way, Chen et al. [10] say that the coatings industry has to be transformed into a "greener" industry by incorporating more alternative renewable raw materials and "greener" technologies into their formulations, once legislation on different countries requires that plastic materials be both degradable as well as biodegradable after their discharge at the environment.

Mechanisms about degradation processes for UV/EB cured inks have been proposed by some authors [11-12]. Bérnard et al.[11] reviewed some results of photodegradation phenomena of resins cured under UV and EB radiations and suggested that, among the many possible candidates, extrinsic chromophores chemical groups formed during processing and curing of samples are the most probable ones to initiate the oxidation of the polymeric matrix. It was observed that radicals are produced via absorption of chromophoric species present in the film and, as the residual acrylates are consumed, there is a concomitant densification of the network through crosslinking reactions. At the end of the process, it is noted that oxygen permeability remains more or less constant and oxidation kinetics becomes almost linear.

Another experiment was performed by Chen et al. [12] through synthetizing soy-based thiols and enes to be cured by UV radiation. It was observed their incorporation to acrylate resin has caused an increasing on the photopolymerization conversion and coating film properties, such as solvent resistance, modulus and elongation, glass transition temperature and thermal degradation temperature.

As discussed by Magagula et al [13], photodegradation processes can aid rapid disintegration of polymers into a powdery residue with a much-reduced visual impact, especially when prodegradant additives are used to enhance their oxo-biodegradation. The central element responsible for the pro-oxidative ability usually belongs to the first transition metal series such as manganese, iron and cobalt as stearates, all of which have the capability to exist in both +2 and +3 oxidation states [14]. In this context, transition metal carboxylates are particularly suitable in which cobalt-, iron-, manganese and cerium-based products have been commercialized [13].

Additionally, it is known that the catalytic effect is stronger for pro-oxidants based on metal combinations capable of yielding two metal ions of similar stability and with oxidation number differing by one unit only [15]. The photodegradation is initiated with the formation of radicals due to the breakup of chemical bonds in the polymer chain. UV radiation in the range of 290 nm to 320 nm is equivalent to the energy required to dissociate C–C and C–H bonds to induce free radicals. The free radicals formed by this cleavage act as initiators for polymer degradation [16]. This abiotic degradation phase increases the biodegradability of the polymer in soil, wastewater, sludge and compost, such as reported by Roy et al. [17].

By this way, this paper aims to investigate the behavior of different UV print inks containing cobalt and cerium stearate under accelerated degradation by means of thermo-analytical methodologies.

Experimental

Materials

The following materials were applied for the preparation of the UV-curable clear formulation:

1. bisphenol A epoxy diacrylate resin (EBECRYL® 3720-TP25, Cytec Industries Inc.) diluted 25% by weight with tripropylene glycol diacrylate (TRPGDA, Cytec Industries Inc.);

2. trimethylolpropane triacrylate (TMPTA, Cytec Industries Inc.);

3. blend of photoinitiators 4,5/3,5/2,0 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, Ciba-Geigy Co.)/2-hydroxy-2-methyl-1-[4-(1-methylvinyl) phenyl] propanone (Esacure KIP 150, Lamberti Co.)/2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one (Irgacure 379, Ciba Specialty Chemicals Inc.), respectively;

4. talc (Nicron® 674, Luzenac America, Inc.);

5. polydimethylsiloxane (Pure Silicone Fluid 100,000cSt, Clearco Products Co., Inc.);

6a,b. polyethylene/polytetrafluoroethylene wax (CeraSPERSE® 164, Shamrock Technology, Inc.).

In order to obtain colored print inks, pigments have been added to the clear coatings, such as the following: 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.) and ruby pigment derived from monoazo calcium salts (Rubide 4B, Hongyan Pigment Chemical Co., Ltd.). The ratio pigment/clear coating was kept constant (21/79 w/w) in order to investigate only the influence of each pigment under UV curing.

It was also used cobalt stearate (CoSt), supplied as pellets by Strem Chemicals Inc. (Newburyport, MA, USA), and cerium stearate (CeSt), supplied as powder by Strem Chemicals Inc. (Newburyport, MA, USA).

Methods

Tests of thermal analysis for cured and uncured print ink samples were performed using simultaneous thermogravimetric analyzer and differential scanning calorimeter SDT Q600 from TA Instruments, New Castle, DE, USA. Around 5 mg pieces from different parts of the samples were placed into platinum crucible and heated at a constant rate of 10 °C min^{-1} from room temperature up to 700 °C under air atmosphere at flow rate of 50 mL min^{-1}.

Results and Discussion

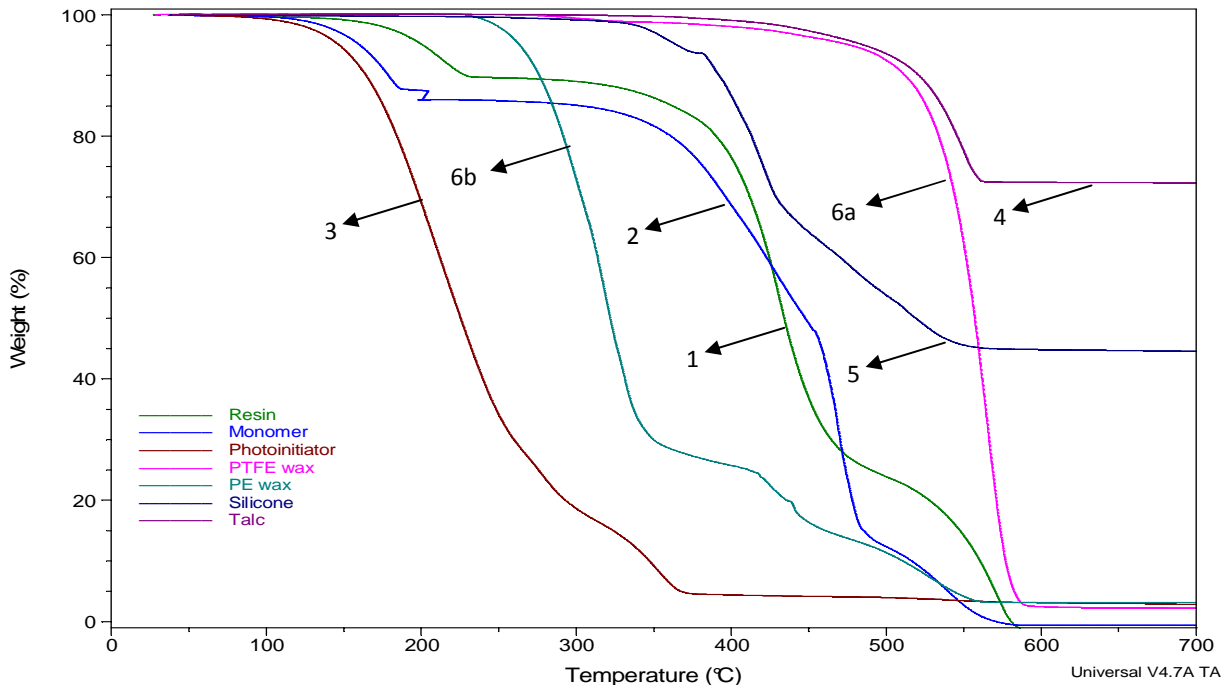Figure 1 depicts the non-isothermal thermogravimetric (TG) curves of the print inks components.

Figure 1 - TG curves showing thermal degradation of print ink components 1 to 6a,b according to Material section description.

By analyzing Fig. 1, it can be seen that some components suffer thermal degradation simply by heat influence, whereas some others undergo chemical reactions before being thermally decomposed. As it can be observed on curve 2, the first step of mass loss occurs at the range of 150ºC up to 200ºC. Under this temperature, the monomer suffers fast polymerization, exothermic reactions, which induces a deformation on the TG curve around 200ºC. The enthalpy of this reaction is high enough to promote the volatilization of a fraction of the sample, inducing a deformation on the TG curve around 200ºC. Additionally, it is important to point out that the studied resin has itself diluted on 25% of monomer, according to supplier information. So, the same thermal behavior can be observed on the curve 1 from the epoxy-acrylate resin, as in the supplied form, in the range of 170ºC up to 230ºC. On the other hand, the product from the thermal curing reaction of the resin is different from the product derived from the thermal curing reaction of the monomer, as it can be observed by the differences between curves 1 and 2 (Fig. 1).

An addendum has to be made about the mass loss from talc sample (curve 4). According to Sánchez-Soto et al. [18], this mass loss may be attributed to water release at lower temperatures, after some grinding time. This result is in accordance with particle size diminution and surface area evolution. It is also discussed that a reaggregation process takes place and probably avoid the water elimination by dynamic thermal treatment throughout larger particles, and thus it causes that water diffusion is more hindered.

Figure 2 and Figure 3 present the thermal behavior of the studied uncured print ink samples as a function of the temperature.
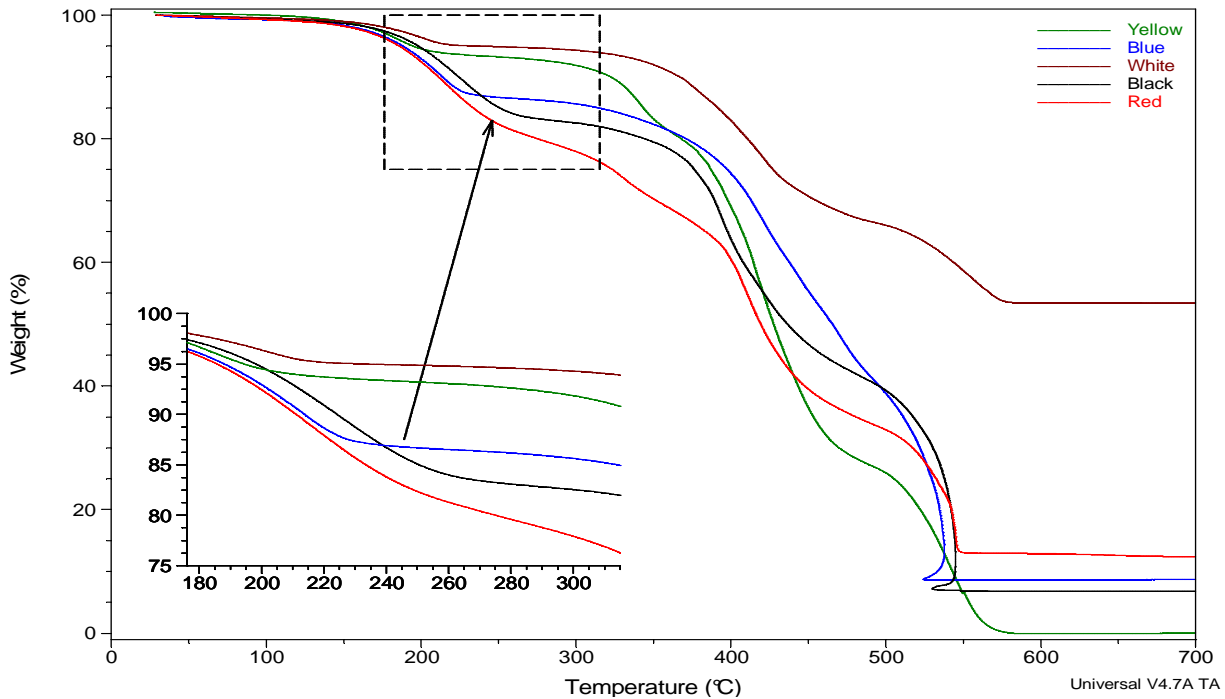
Figure 2 - TG curves for studied uncured print inks.

By analyzing Figure 2, it can be seen that the compositions present different profiles of mass loss which can be clearly attributed to the different origins of the pigments once the ratio clear coating/pigment was let constant for all samples. Additionally, all studied uncured samples present at least three different thermal events:

- in the range of 150°C up to 290°C, which corresponds to volatilization of components, mainly photoinitiator and monomer, during thermal curing reaction, as previously described. This event just occurs because these compositions are proposed to be cured by radiation technology, more specifically UV light, not by heat, which state-of-art says that no volatile components are produced during UV curing reaction.

- from 310°C up to 450°C, corresponding to the thermal degradation of the so-formed cross-linked network by thermal curing, as suggested by Alves et al. [19] and Kim et al. [20].

- from 500°C up to 580°C due to the conversion of carbonaceous residue to carbon dioxide.
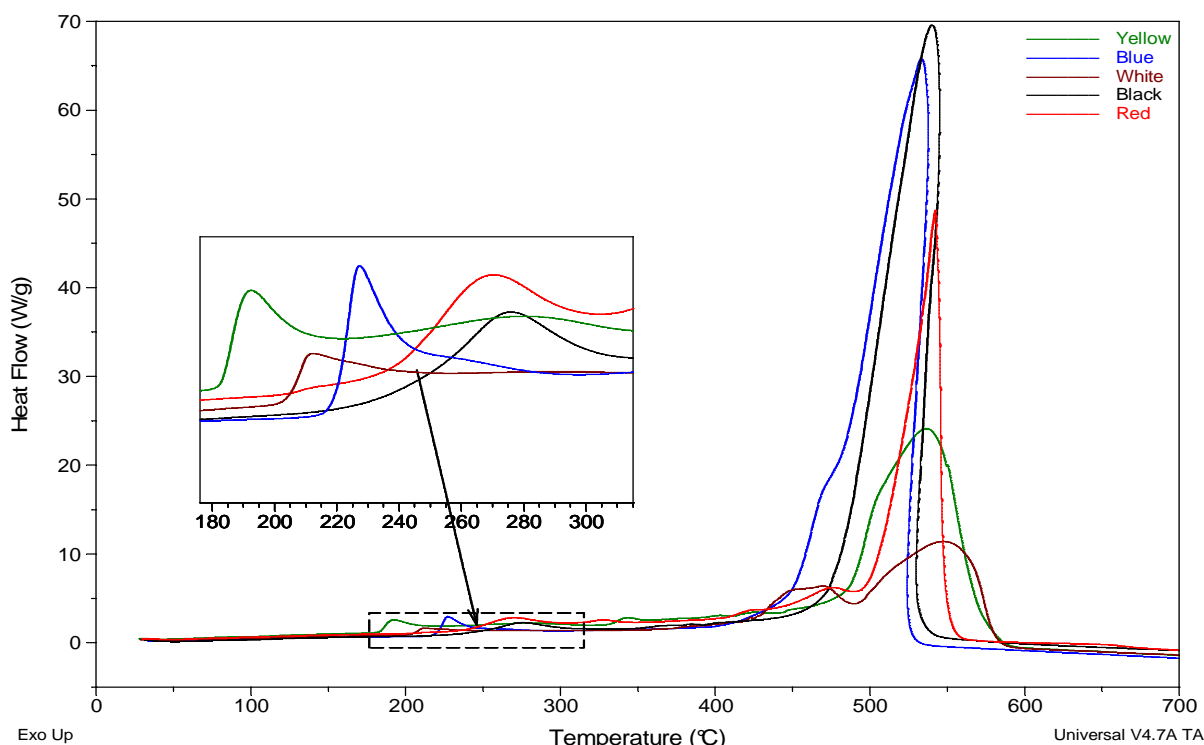
Figure 3 - DSC curves for studied uncured print inks.

Concerning the steps of thermal degradation of the studied print inks, the idea of mass loss during thermal curing can be proved if we also analyze Fig. 3 on the temperature range of 150-290°C. It can be seen that each composition presents an exothermic peak on this temperature range, resulting from concomitant exothermic thermal curing reaction and endothermic volatilization event, which extension is dependent on the pigment chemical family. Some more detailed discussion about the influence of thermal curing on UV-curable compositions is presented by Ruiz et al. [21]. So, in order to achieve more details about this thermal behavior, simultaneous DSC/TG (SDT) curves were obtained for pristine pigments and studied uncured print inks, which are shown on Figure 4.

SDT analysis presented of Fig. 4 allows us to observe that, in fact, thermal degradation is greatly influenced by the pigment incorporated to the clear coating. If we note, for example, that yellow pigment already presents an exothermic peak at the aforementioned temperature range, so it is necessary to subtract this enthalpy in order to obtain the real curing enthalpy. As this is not accurate, we choose to continue our discussion just based on the white print ink, which corresponding pigment has higher thermal stability.

So, two pro-degradant additives were incorporated to the white print ink in order to evaluate a possible increasing on the accelerated degradation rate of the samples before/after UV curing.

By this way, Figure 5 presents the thermal degradation behavior from white print ink, thermally cured as function of linear increasing of temperature inside the SDT furnace, and UV-cured at 200 mW cm^{-2}, without or with cobalt stearate or cerium stearate.
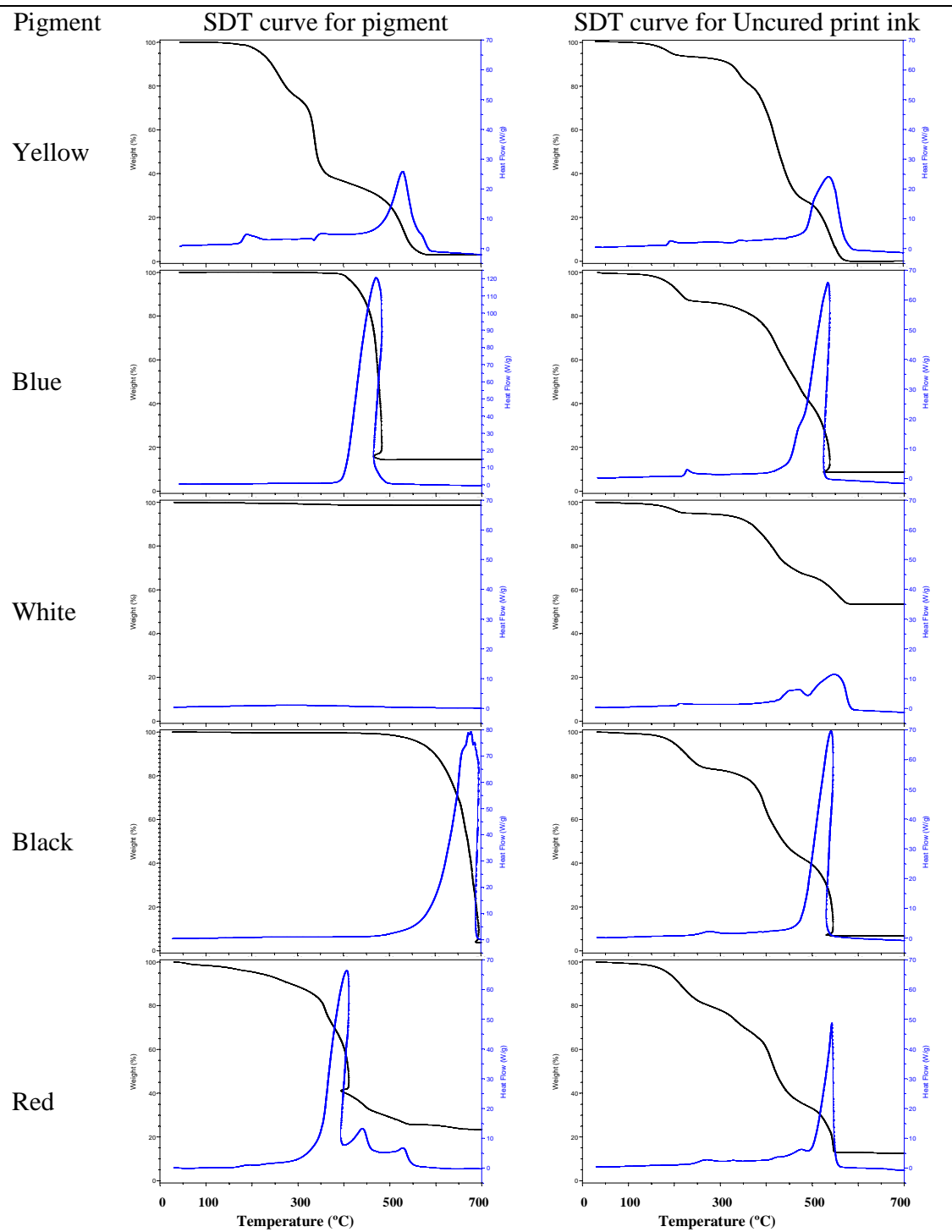
Figure 4 - SDT curves for pigments and uncured print inks.

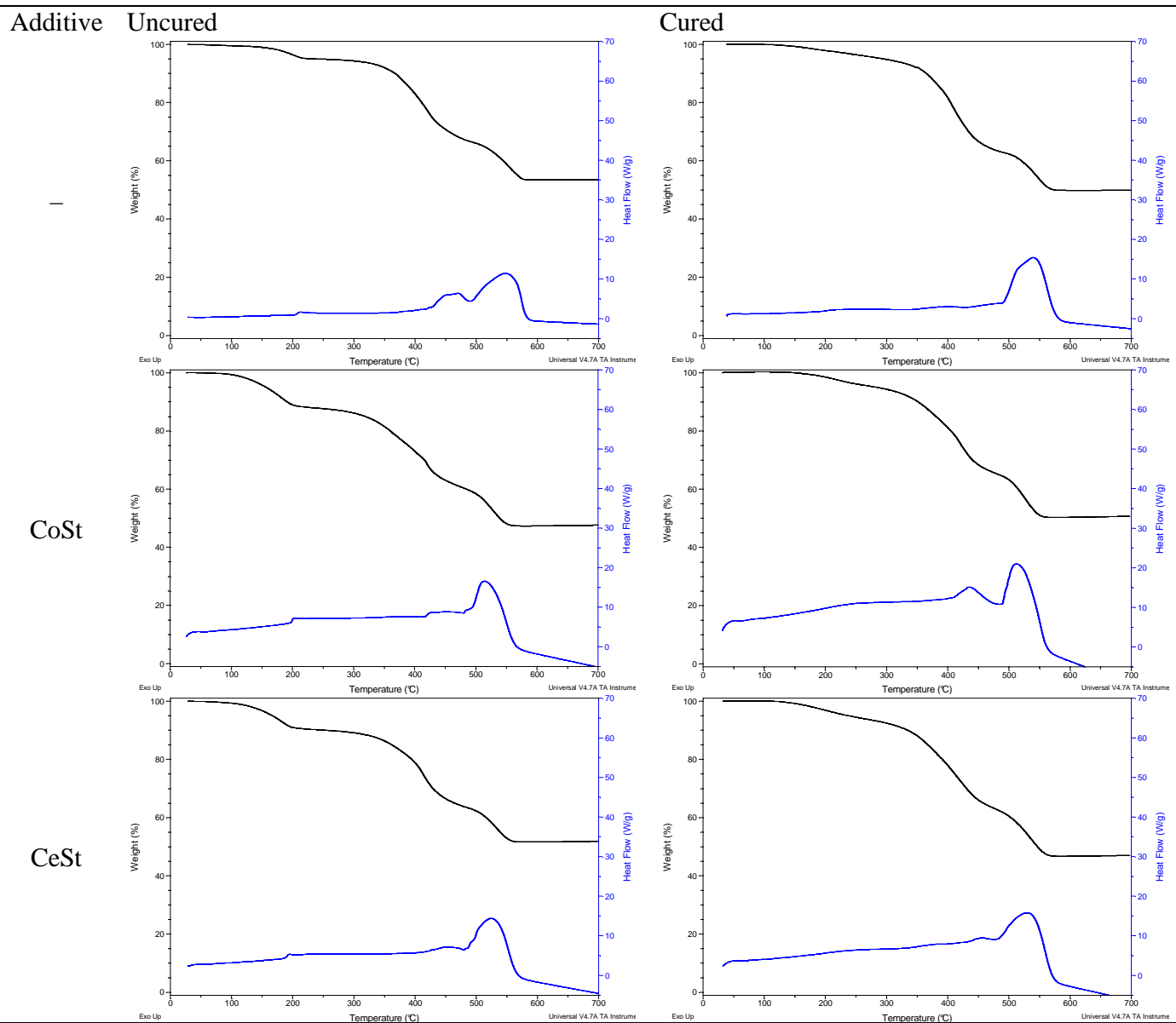| Additive	Uncured	Cured

Figure 5 - SDT curves for uncured and UV-cured white print inks, containing or not CoSt or CeSt.

Table 1 presents the values for the onset degradation temperature measured by tangent method associated to the second event of the TG curves from thermally-cured and UV-cured white print ink samples.

According to Figure 5, the presence of CoSt or CeSt has not influenced the thermal curing behavior of the studied print ink, probably due to the thermal decomposition of the metallic stearates, as illustrated in Figure 6.

Table 1 - Onset degradation temperature for the different studied compositions

| Sample	Onset degradation temperature (°C)
Thermally cross-linked resin	391
Thermally cross-linked monomer	362
Thermally cured white print ink	370
UV cured white print ink	353
Thermally cured white print ink containing CeSt	342
UV cured white print ink containing CeSt	340
Thermally cured white print ink containing CoSt	339
UV cured white print ink containing CoSt	324
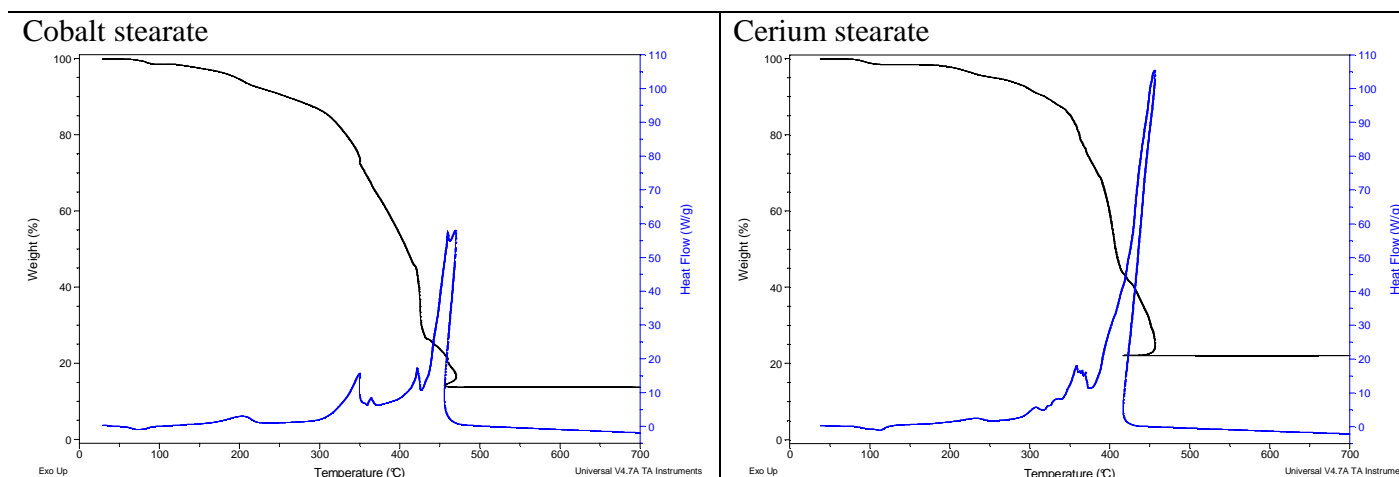
Figure 6 – SDT curves from the pro-degradant agents.

Furthermore, the samples containing pro-degradant agents, which were previously cured by UV light, presented a meaningful reduction (around 30°C) on thermal stability when compared to the stability of thermally-cured and unmodified sample (without pro-degradant agent).

It is observed that the thermal stability for the cured white print ink remains roughly the same as the uncured one.

The most remarkable changes are observed for the onset degradation temperature corresponding to the degradation of the polymeric network (Tab. 1), as it was previously discussed. If we consider that both components resin and monomer have an average onset degradation temperature around 375°C, we will note that this value is roughly the value for the onset degradation temperature of the thermally-cured white print ink. When this composition is UV-irradiated, it is observed a reduction on this temperature, indicating that the sample is more susceptible to accelerated degradation. The same behavior is observed for formulations containing CoSt and CeSt, but in a highlighted way, indicating the pro-activity of the agents to catalyze the thermal degradation of the UV-cured white print ink studied samples.

Conclusion

The accelerated degradation by temperature has shown to be able to activate the catalytic ability for chemical bonding rupture of the polymeric components in the studied print inks after UV curing, as it happens when applied to more conservative polymer systems, especially polyolefins. Other analytical techniques will be used to clarify the comprehension of chemical degradation mechanisms induced by metallic stearates.

Acknowledgments

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