Studies on UV and thermally radical induced cross-linked polymer networks as charge-transport layers in electrophotographic coating applications

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Abstract

A number of both UV and thermally radically induced cross-linked epoxy acrylates and vinyl polymers/copolymers (cross-linked with divinyl benzene) have been prepared and predoped with different charge-transport media (CTM) and examined as alternative potential durable wear resistant charge-transport layers (CTL) for electrophotographic applications. The CTMs studied were tri-*p*-tolylamine (TpTA), 2,5-bis(4-diethylaminophenyl-1,3,4-oxadiazole) (OXD), *p*-diethylaminobenzaldehyde-diphenylhydrazone (DEH) and *p*-diethylaminophenyl benzaldehyde methylphenyl hydrazone (T191). The polymer binders were based on epoxy acrylates, epoxy resins (amine cured) and divinyl benzene cross-linked styrene/styrene-*co*-methyl methacrylate, styrene–allyl methacrylate and poly(vinyl cinnamate) and compared with the properties of a conventional polycarbonate CTL. The structure of the cross-linked polymer, nature of the CTM and its concentration controlled the extent of cross-linking and mobility of charge within the coating. UV cured systems were found to fail as CTLs due to the presence of high levels of hydroxy groups on the polymer backbone, residual initiators and photosensitivity and photolysis products of the CTM's trapping and inhibiting charge migration. Polymers containing styrene units, on the other hand, display good charge transport properties compared with polycarbonate due to strong interactions of the pendant phenyl groups stabilising the cation radicals produced on illumination. However, these coatings, although hard were found to be brittle in nature. Copolymerisation with methyl or allyl methacrylate reduced the brittleness but also the mobility of charge due to spacing of the phenyl rings along the polymer network. Thermal cross-linking of a polymer that undergoes a 2+2 cycloaddition, poly(allylcinnamate), gave a hard tough coating that exhibited promise as an effective CTL when compared to that of polycarbonate.   © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since the early discovery of electrophotography by Carlson [1], there have been considerable developments in the nature of the materials utilised as photoreceptors, although the principle remains essentially the same. Chalcogenide glasses based on alloys of selenium with tellurium were amongst the first commercial systems to be developed [2,3]. However, with increasing costs, problems in fatigue and toxicity these materials were eventually replaced by organic substrates [2,3]. The latter were more cost-effective and versatile in copier applications. Following the shortlived single layer photoreceptors dual layer systems have become the acceptable norm comprising a lower charge generation layer

(CGL) and an upper charge transport layer (CTL) [2,3]. The main advantage of dual layer photoreceptors is that they allow optimisation of both charge generation and charge transport with improvements in spectral sensitivity and process lifetime [2,3]. The CGL is often prepared by dispersing a microcrystalline pigment in a polymer host and then coating onto a substrate using solvent-casting techniques. The pigment structures and form vary, one of the most common being a metal free phthalocyanine [4]. The CTL also utilises molecularly doped polymers consisting of a hole transport compound (arylalkylamines, arylamines, hydrazones and pyazolines) in the order of 50% by weight in a polymer host such as polycarbonate [2,3,5].

These transport molecules must have good solubility and compatibility with the polymer host and coating solvent. The transport formulation should also exhibit good film forming properties and there should be a high efficiency for the injec-

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tion of charge into the transport material from the site of photogeneration. Thus, the transport of charge must proceed without substantial mobility limitation. It is also desirable that there should be negligible residual surface potential at the time the electrostatic latent image is developed, since the development time is determined by the timing of the exposure-development process. Any residual potential could be due to the presence of traps or impurities from the manufacture or photochemical instability of the CTL materials. Corona-induced chemistry may also take place. Synonymous with this is the fact that photoreceptors may undergo a change in xerographic sensitivity upon extended cycling. This is often manifested as a decrease in charge acceptance and higher dark discharge rate or an increase in the residual potential [2,3]. This fatigue behaviour strongly influences the photoreceptor performance and lifetime. Mechanical stability is also an important factor with the organic polymer binder experiencing severe wear problems on continued cycling.

It this paper, we have undertaken an extensive study on the viability of a series of cross-linked polymer hosts as potential CTL photoreceptors to replace standard thermoplastics such as polycarbonates. Both UV and thermally radically induced cross-linked Bisphenol-A epoxy acrylate and vinyl monomers were chosen for study. In the latter case cross-linking was effected through the use of divinylbenzene as a comonomer. Poly(allyl cinnamate) was also assessed due to its different mode of cross-linking via a $2+2$ cycloaddition process to give cyclobutane structures. This polymer will also cross-link via the allyl group to produce a tough yet flexible material. Poly(vinyl cinnamate) was slightly brittle. In each case it was important to assess the charge-transport characteristics in comparison with those of a typical doped polycarbonate CTL. In all cases the structure of the final polymer is crucial in terms of hole mobility. Thus, a Bisphenol-A epoxy acrylate was chosen for the UV study due to the Bisphenol-A origins of polycarbonates. It is also widely understood [2,3] that polymers with phenyl side groups show much higher mobility than polycarbonates. In this regard the vinyl monomers chosen were styrene and divinylbenzene. Poly(allyl cinnamate) also possesses phenyl side groups.

2. Experimental

2.1. Materials

The CTMs used in this study namely, tri-p-tolylamine (TpTA), 2,5-bis(4-diethylaminophenyl-1,3,4-oxadiazole (OXD), p-diethylaminobenzaldehyde-diphenyl hydrazone (DEH) and p-diethylaminophenyl benzaldehyde methylphenyl hydrazone (T191) were supplied by GBL, Byfleet, Surrey. Commercial photoinitiators, Irgacure 1700 (25% Bis(2,6-dimethoxybenzoyl)-2,4,4'-trimethylpentyl phosphine oxide + 75% 2-hydroxy-2-methyl-1-phenylpropan-1-one), Irgacure 369 (2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one), Irgacure 907 (2-methyl-1-(4-

methylthio)phenyl)-2-morpholino propan-2-one) and Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone) were supplied by Ciba-Geigy, Manchester (UK), Lucirin TPO (Acylphosphine oxide) by BASF, Germany, ITX (2-isopropoxythioxanthone) by Great Lakes Fine Chemicals, Widnes, UK and camphorquinone by Aldrich Chemical, UK. The bisphenol-A epoxy acrylate (Actilane 420), hexane diol diacrylate (HDDA), diethylene glycol diacrylate (DEGDA), triethylene glycol diacrylate (TEGDA) and trimethylpropane triacrylate (TMPTA) were all supplied by Akcros Chemicals, Manchester, (UK). The n-butyl acrylate, styrene, methyl methacrylate, allyl methacrylate, allyl cinnamate, benzoyl peroxide, lauryl peroxide, azobisisobutyronitrile (AIBN), diethyl ether, tetrahydrofuran, toluene, bisphenol-A, epichlrohydrin, cyclohexanone, dichloromethane, methanol, sodium hydroxide, potassium hydroxide and magnesium suphate (anhydrous) were supplied by Lancaster Synthesis, UK. The bisphenol-A polycarbonate (Lexan 161) and polycarbonate-Z were supplied by GBL, Surrey, UK. Metal free phthalocyanine was obtained from Zeneca Specialties, Manchester and was used as a dispersion in poly(vinyl butyral) obtained from BASF, Germany.

2.2. Purification methods

All solvents except tetrahydrofuran (THF) were distilled over nitrogen before use and then dried over molecular sieve type 4A (Aldrich Chemical, UK). THF was refluxed over sodium in the presence of benzophenone under nitrogen for 5 hours followed distillation, filtration through silica gel, micro-filtered and then dried over sodium wire. The AIBN was recrystallised from toluene and dried under vacuum at 40°C. The styrene, butyl acrylate, methyl and allyl methacrylates were purified to remove inhibitor by washing three times with 2 M sodium hydroxide and then washing with distilled water until all alkali was removed. They were then dried over anhydrous magnesium sulphate followed by distillation under nitrogen.

2.3. Thermal polymerisations

The required monomer composition weights were transferred to a multi-necked flask with 0.1% of initiator. The monomers were then degassed by freeze-thaw cycles until a vacuum of 1.8×10^{-3} mbar was obtained. After degassing nitrogen gas (>5 ppm O_2) was bubbled through the monomer followed by heating for an appropriate time at 80°C in an oil bath. Conversions were controlled so as to provide viscous (but not gelled) partially polymerised systems that could be easily applied as coatings for the CTL. The CTM (at the appropriate level) was then incorporated before application using a draw down K-bar (R.K. Print Coat Instruments, UK).

Photopolymerisation of the monomers/co-monomers was undertaken by irradiation of the flask using a 400 W high pressure mercury lamp until a suitable viscosity for coating

was obtained (prior to gelation). All photoinitiators were used at 4% w/w on the monomer system. This was essentially a highly subjective judgement since all coating layers as CTLs were eventually cured by oven heating.

2.4. Synthesis of epoxy resin

Bisphenol-A (45.6 g) and epichlorohydrin (185 g) were dissolved in a suitable reflux set-up with mechanical stirring. The reaction mixture was heated to 80°C followed by the addition of sodium hydroxide (16 g) keeping the reaction temperature below 100°C. After 45 minutes of refluxing the unreacted epichlorohydrin was removed by vacuum distillation followed by filtration to remove the salt. The thermal curing of the epoxy resin is undertaken at 90°C by using triethylamine at up to 15% w/w of the resin.

2.5. CGM layer

The CGL was prepared by dissolving poly(vinylbutyral) (1.0 g) in 40 cm^3 of cyclohexanone followed by the addition of metal free phthalocyanine (1.0 g). The mixture was then thoroughly dispersed using a shaker overnight. The dispersion was then coated onto an aluminised poly(ethylene terephthalate) film using a K-bar No. 2 and then covered with a glass plate 5 mm from the film surface in a dust free box. After solvent evaporation the film was then dried in a hot air oven at 80°C for 1 h to give a film thickness of 0.5 μm.

2.6. CTM layer

The CTL was prepared by dissolving the appropriate polymer (or prepolymer) binder (3.0 g) in 8 cm^3 of THF or dichloromethane followed by the addition of the CTM (2.0 g) and then stirring for 12 hours. The resulting solution was then coated on top of the CGL using K-bar No. 8 to achieve an eventual dry film thickness of 16–20 μm.

2.7. Absorption spectra

Absorption spectra of the CTMs and photoinitiators were obtained using a Perkin-Elmer Lambda-16 spectrophotometer.

2.8. Infrared spectral measurements

Fourier transform infrared spectra were obtained using a Biorad FTS-7 spectrometer. A reflection accessory was used to measure the infrared spectra of films by monitoring the carbon–carbon double bond vibrations at 1630 and 810 cm^{-1}.

Measurements on real-time were also obtained. Here the initiators were dissolved in a minimum quantity (2–3 cm^3 of tetrahydrofuran) followed by mixing with a prepolymer or monomer mixture. Traces of solvent were then removed by flushing with argon for 30 min.

The resin was then placed between pieces of low-density polyethylene using a separator to give a film thickness of 50 μm. The polyethylene holder was then placed between two infrared salt plates and placed in the sample beam. Two polyethylene film samples were used as the reference. The decrease in absorbance at 1638 cm^{-1} of the vinyl absorption band was then monitored using a Perkin-Elmer 842 dispersive infrared spectrometer in real-time mode during irradiation using a fibre optic arrangement. The irradiation source used here was an ILC 302UV (Laser Lines, Beaumont Close, Banbury, Oxon, UK) (150 W Xenon, 200 nm, infrared) switchable between UV and visible light with a cut-off point at 400 nm. The UV energy up to 400 nm was measured at 150 mW/cm^2. Plots of percentage conversion with time were obtained from which second plots of mol l^{-1} vs. time in seconds were obtained. From the initial slopes of the second plots Rp values (mol l^{-1} s^{-1}) were obtained.

2.9. Gel content

Gel contents were obtained by stirring the polymer in toluene for 3 hours followed by filtration through a pre-weighed glass wool filter. Gel weights after air drying in an oven at 60°C were then measured.

2.10. Differential scanning calorimetry (DSC)

Glass transition temperatures were obtained where possible using a Perkin-Elmer DSC 7 system.

2.11. UV curing equipment

The CTL's were photocured using a Uvalight minicure system (Horn Lighting, Birmingham, UK) utilising exchangeable 400 W high pressure mercury/metal halide doped lamps.

2.12. Sheen pendulum hardness

Hardness measurements were obtained using a Sheen pendulum hardness instrument (Sheen Instruments, UK). The surface hardness is measured by the ability of the film produced to dampen the oscillations of a swinging pendulum system through two 5 mm hemispheres resting on the film surface. Pendulum movement is monitored by an electronic impulse sensor and electronic counting device.

2.13. Xerographic measurements

A xerographic apparatus was built to replicate the actual process in a copying machine. These techniques are widely used to characterise the photoconductive properties of the photoreceptors.

2.14. Xerographic apparatus

The photoreceptor, coated onto the aluminised polyester was fixed around an aluminium drum using conductive adhesive tape. The aluminium drum was then mounted onto a turn table so that the drum was close to the surface of the corona wire as possible. Caution was exercised that no part of the drum was physically touching the corona wire. A probe powered by an external power supply was placed close to the surface of the rotating photoreceptor to measure the surface potential. The photoreceptor drum was rotated at 25 rev s^{-1} to check that the photoreceptor was rotating freely without touching any of the components fixed around the drum.

The apparatus lid was then closed so that no external light could interfere with the measurements. The photoreceptor was then initially exposed to halogen light (100 W) to remove any charges deposited on the surface. The photoreceptor was allowed to rotate and the surface was charged as the drum passed the corona, the amount of charge deposited on the surface was then measured by the probe. After each charging cycle the drum passed the erasure light to remove any excess charge from the surface of the drum before the next cycle. This procedure was performed for a number of cycles. The discharge characteristics of the photoreceptor were then measured by exposing the photoreceptor to visible fight after charging. The charging and discharging readings were displayed on a digital voltmeter and also on a chart recorder or storage oscilloscope.

2.15. Time of flight measurements (TOF)

Time of flight techniques are widely used to study the drift mobilities in highly resistive materials. In the experiments undertaken in this work carriers are injected into the sample, sandwiched between two metal electrodes. The top surface of the sample was exposed to a short pulse of radiation (much shorter than the transit time of the carriers) to generate free carriers of both signs in equal concentration at one end of the film. The polarity of the applied field determines the sign of those carriers which drift across the sample. For example, in hole transport the negative carriers (electrons) are rapidly extracted from the drift space via the positively biased top electrode under the influence of the bias field. As photogenerated carriers drift through the film under the influence of the applied field, their flux (as current) was measured and displayed on the oscilloscope. When carriers reach the lower electrode, the current ceases to flow and the transit time can be read from the transit waveform. The excitation is usually small enough, that the amount of injected charge does not perturb the internal field in the sample (i.e., carriers always experience the same field). This condition is termed the 'small signal mode'. The experiment can only be performed with high resistivity materials where free carriers do not screen the injected charge or cause recombination. In other words the dielectric relaxation time must be long compared to the transit time, i.e.,

$$t_{tr} \ll \tau_d = p \varepsilon \varepsilon_0$$

where p is the dark resistivity, ε is the relative permittivity of the solid and ε_0 is the permittivity of free space. Since the current flows only while the carriers are drifting in the material from the time it takes for the carriers to arrive at the substrate, the drift mobility can be derived.

$$\mu = L^2 / V \cdot t_{tr}$$

were L is the film thickness, V is the voltage across the sample and t_{tr} is the transit time. If the carriers do not recombine and arrive at the lower electrode without any trapping, the current would have a square shape. However, in reality the carriers experience trapping, and the measured waveform is far from ideal. Also the mobility can change throughout a non-uniform film. However, the shape of the wave offers much information about the transport processes in the material.

2.16. TOF apparatus

In the TOF apparatus the film sample is sandwiched between two metal electrodes and placed in a sample holder. The temperature was controlled by two heating elements inserted in the copper block of the sample holder. If necessary the cooling of the sample was performed by using the cold finger dipped in liquid nitrogen. Two thermocouples were used to monitor the temperature, the first was placed immediately beside the sample and the second was placed inside the copper block. This allows accurate temperature control in the experiments. The bias voltage on the top electrode of the sample was obtained from a Brandenburg: 475R regulated power supply. The signal was detected by directly connecting the bottom electrode to the input current amplifier. The amplified signal was then captured via a storage oscilloscope.

2.17. Procedure for transit time measurements

Once the sample was sandwiched between two electrodes its capacitance and resistance was measured to check that a good contact was established between the sample and the electrodes. The cryostat was closed and the pressure was taken to 5×10^{-5} Torr. Room temperature TOF measurements were taken where, starting at low fields, the bias voltage was increased in 10 V increments until 150 volts was reached and then 100 V increments until 1.4–1.5 kV is attained. Once the scan was completed the results were checked by returning to low fields and then taking further measurements to show that no change in the result had taken place. Measurements at various temperatures may also be performed. This is usually performed by first taking measurements at reduced temperatures and then incrementally increasing the temperature as desired. Time of flight set-ups and reviews on the subject are covered elsewhere [6,7].

3. Results and discussion

3.1. Epoxy acrylate systems

The first and most important factor to consider when designing CTL's for UV curing is the efficiency of the conversion process to yield a hard non-tacky coating with effective through cure. This relies heavily on the competitive absorption of the CTL system with regard to that of the photoinitiator for light energy from the excitation source. In turn, this normally depends upon the emission spectrum of the excitation source. Thus, should the CTL or CTM absorb significantly where the initiator absorbs then activation and curing of the coating is expected to be inhibited. The absorption spectra of the four CTM used in this study are shown in Fig. 1 for THF solvent. They all absorb strongly in the region 200–400 nm. At 40% w/w of CTM, normally used in commercial practice then one can reasonably argue that excitation of an initiator in this region will be completely inhibited. Most photoinitiators absorb strongly in this region of the spectrum. An examination of a range of photointiators used in this study showed that only the Irgacure 1700 exhibited a long wavelength tail beyond that for the four CTMs, i.e., up to 450 nm. For effective through cure 3% w/w of Irgacure 1700 was required in this work.

When considering the cross-linked density of the epoxy acrylate system factors such as monomer functionality and the compatibility of the CTM need to be examined. Indeed, these are important factors throughout this study. For viscosity control a diluent monomer is used in conjunction with the epoxy acrylate prepolymer often up to 40% by weight. Using 20% of diluent monomer the rate of photocuring was found to follow the order TEGDA > TMPTA > HDDA > DEGDA > n-BA. This order essentially follows the decrease
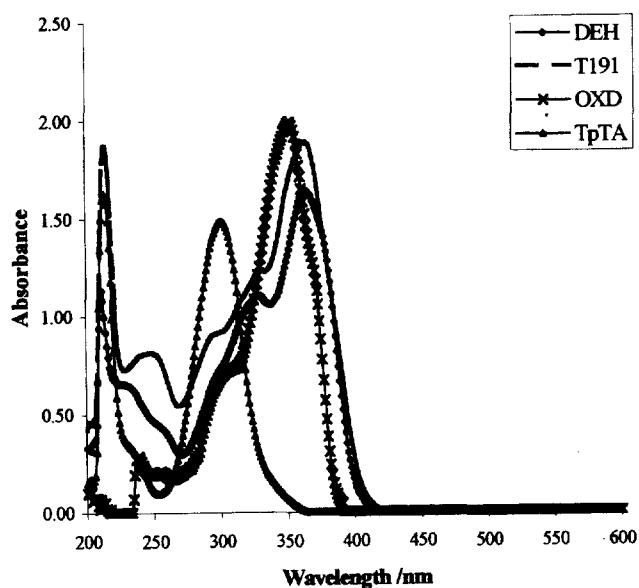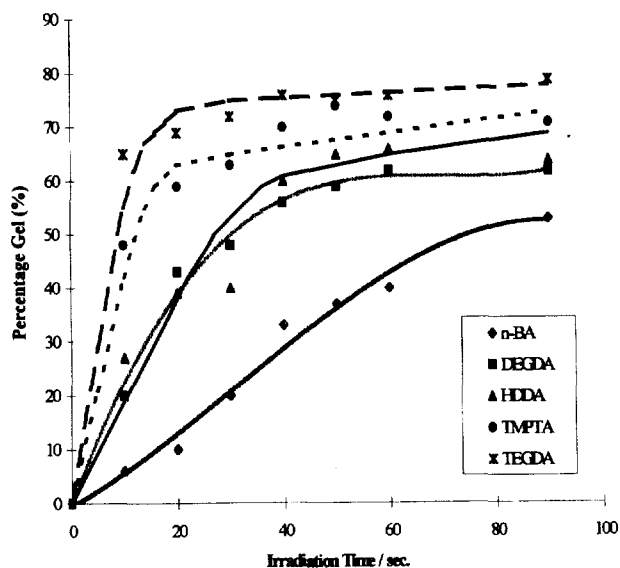

Fig. 2. Percentage gel versus irradiation time (s) (400 W Hg) for an epoxy diacrylate prepolymer with 20% w/w of (♦) n-BA, (■) DEGDA, (▲) HDDA, (●) TMPTA and (X) TEGDA.

in reactive acrylate functionality of the monomer with the monofunctional n-BA having the least effect. The only exception is the diluent TEGDA which is bifunctional. Compatibility and reactivity are also important functions. Plots of percentage gelation versus irradiation time are shown in Fig. 2 where the same trend in photocuring is followed. Surprisingly, the effect of percentage of each diluent had little effect on the photocuring rate so on this basis in order to maximise the viscosity of the CTL a 20% w/w of TEGDA was selected. The effect of the CTM at 40% w/w is also an important factor to be considered. Percentage conversion rates measured by FTIR for the depletion in double bond content are shown in Fig. 3. It is seen that both T191 and DEH markedly inhibit the curing reaction whereas both TpTA and OXD have little effect on the conversion. This appears to be consistent with
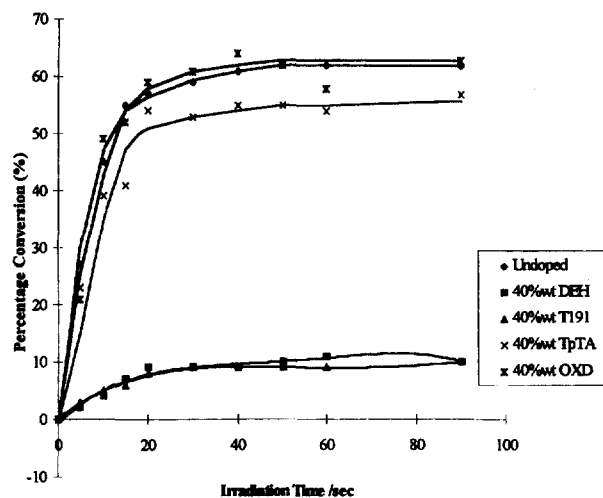

Fig. 1. Absorption spectra of CTMs (- ♦ -) DEH, (- -) T191, (- X -) OXD and (-▲-) TpTA at 10^{-5} M in THF.

Fig. 3. Percentage conversion of epoxy diacrylate formulation (20% w/w TEGDA) on irradiation (400 W Hg) (♦) without and with 40% w/w of (X) TpTA, (X) OXD, (■) DEH and (▲) T191.
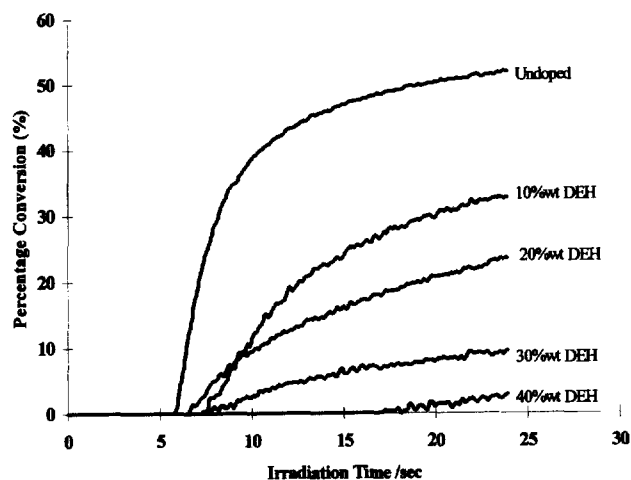
Fig. 4. Percentage conversion of epoxy diacrylate formulation (20% w/w TEGDA) on irradiation (400 W Hg) without and with 10, 20, 30 and 40% w/w of DEH.

the slightly longer wavelength absorption spectra of the former CTMs screening out the absorption by the photoinitiator (Fig. 1). Concentration effects on the photocuring rate have also been examined and are shown in Fig. 4 for the DEH CTM. A strong reduction in the curing rate is seen over the 40% w/w concentration range by this particular molecule.

In order to maximise the photocuring rate lamps with a stronger visible light component were also examined. Comparative data are shown in Table 1 for iron and gallium doped lamps. These showed a 10% increase in cure rate which was insufficient to minimise the cure time. Other problems were also encountered with the use of the CTMs in the epoxy acrylate. The first, is that the TpTA was incompatible with the epoxy acrylate resin. The dipole moments of TpTA, DEH, T191 and OXD are 0.56 D, 3.24 D, 3.44 D and 2.56 D, respectively [8]. Thus, on curing the TpTA is unable to align itself in the cured matrix and crystallises out on the surface of the coating. The second problem is the observed reduction in the Tg of the cured coating with increasing concentration of CTM. Due to problems with the other three CTMs only the OXD could be examined in this regard. The data are shown in Table 2 where it is seen that the Tg (DSC) of the epoxy acrylate is markedly reduced with increasing OXD concentration. Thus, at 40% w/w using the pendulum hardness method a typical polycarbonate coating with 40% of DEH (commercial) has a value of 220 while an epoxy acrylate coating with either DEH or OXD at the same level has a value of 270 ($\pm$10) (Table 3). Similar data and problems were also found for the thermally cured epoxy acrylate resin. In this case triethylamine was used as the curing agent. Maximum cure was obtained at 10% w/w of amine, thereater it decreased.

The crucial factor is the ability of the coating to transport charge. To measure this property dual layer systems were prepared where the CTL is overlaid onto a standard CGL of metal free phthalocyanine. Using the electrophotographic device a surface potential is applied to the coating ($-$ve)

Table 1
Influence of irradiation source on %conversion of an epoxy acrylate: TMPTA resin (80:20 w/w) containing 40% w/w of DEH after 30 s of irradiation

Irradiation source	% Conversion
Hg	8
Fe-doped Hg	18
Ga-doped Hg	18

Table 2
Influence of CTM (OXD) concentration on the T_g of an epoxy acrylate: TMPTA resin (80:20 w/w) after 60 s of irradiation using a high pressure Hg Lamp (400 W)

% OXD	T_g
0	256
10	218
20	154
30	139
40	123
50	105
100	74

Table 3
Sheen pendulum hardness oscillations for the different CTLs with 40% w/w of OXD

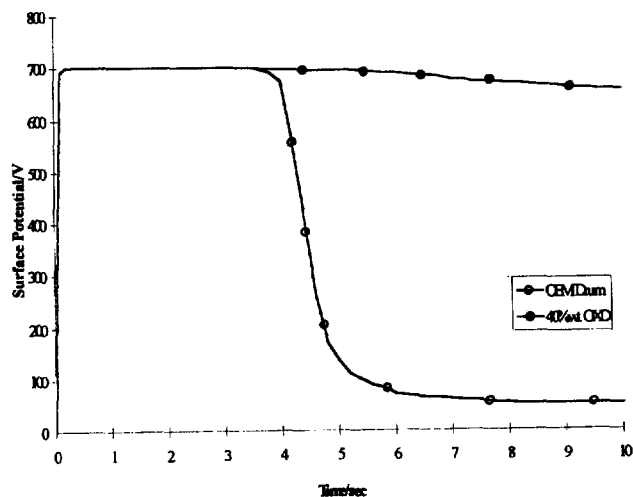| CTL	Oscillations ($\pm$10)
Polycarbonate	220
Epoxy diacrylate: TEGDA (80:20)	270
Styrene-co-divinyl Benzene (10%)	180
Styrene-co-DVB (10%)-co-MMA (30%)	205
Poly(allyl cinnamate)	270

Fig. 5. Charge-transport showing surface potential ($-$ve) with time of a commercial polycarbonate CTL (O) and (●) an epoxy acrylate (thermally and photocured) coating with 40% w/w of OXD.
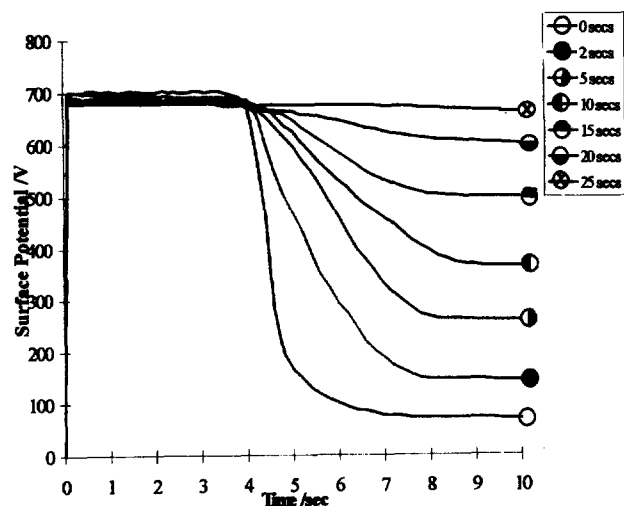
Fig. 6. Charge-transport showing surface potential (−ve) with time of a commercial polycarbonate CTL coating with 40% w/w of OXD (○) before and after (●) 2, (circle half-filled right) 5, (circle half-filled left) 10, (circle half-filled up) 15, (circle half-filled down) 20 and (crossed circle) 25 s of pre-irradiation with a 400 W lamp.

and then exposed to light to generate carriers that deactivate the surface potential. This process is seen as a rapid drop in surface potential with time. However, all the photo and thermally cured doped epoxy acrylates failed to discharge as shown by the graph in Fig. 5. While a typical commercial drum coating is seen to discharge rapidly the epoxy acrylates failed. This result is consistent with that of Vannikov et al. [8] who found that the polarity of the binder strongly influences the charge-transport in the material.

Photolysis of the CTL is also a major problem giving rise to products which will behave as traps preventing hole transport. This effect is shown in Fig. 6 for a typical polycarbonate-Z CTL with 40% of DEH which has been pre-exposed to the 400 W light source for different periods of time. The charge transport is seen to decrease with prior irradiation time due
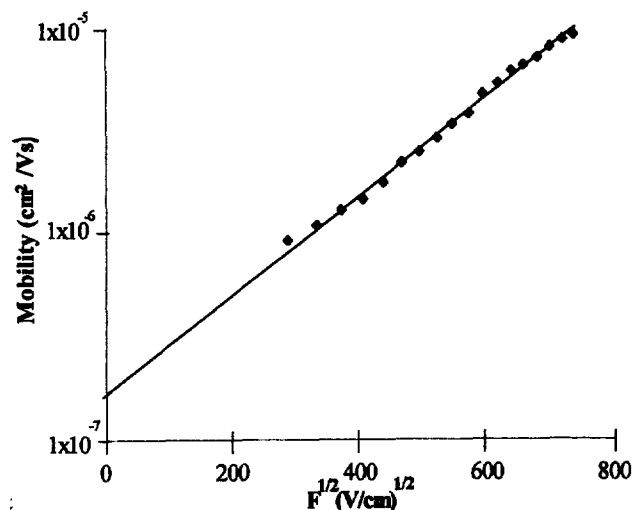
to the instability of the CTM. The high polarity of the epoxy acrylate resin may also cause deep trapping [8] due to the presence of strong polar groups in the network.

Time of flight (TOF) measurements also determines the ability of the coating to transport holes. TOF measurements were carried out at room temperature under vacuum and plots are obtained for hole mobility versus the square root of the applied field. A typical plot for future reference is shown in Fig. 7 for a polycarbonate CTL with 40% w/w of DEH. This result is in agreement with published data [2]. Unfortunately, none of the epoxy acrylate systems developed exhibited hole mobility by TOF and is consistent with the findings of Pacansky et al. [9–11] on UV cured systems for CGLs.

3.2. Vinyl polymer coatings

3.2.1. Styrene–DVB

The first system examined was based on a styrene–divinyl benzene mixture. In the first instance, the use of peroxide initiators for thermal curing were found to be detrimental to the CTM. The DEH for example, turned bright orange due to oxidation by the peroxide. Future work was therefore, based on the use of AIBN as the initiator. No discoloration was found under this condition. To high a ratio of DVB caused an uncontrollable reaction and heavy gelation. Thus, admixtures of DVB up to 20% were examined. Conversion rates by FTIR are shown in Fig. 8 at 80°C. The rate is seen to increase with increasing DBV content and achieves a maximum at 20% w/w, thereafter levelling out. In fact, the hardness of the coating by pendulum hardness was found to be a maximum at 10% w/w of DVB and allowed ease of handling for coating of partially cured systems. This ratio was used
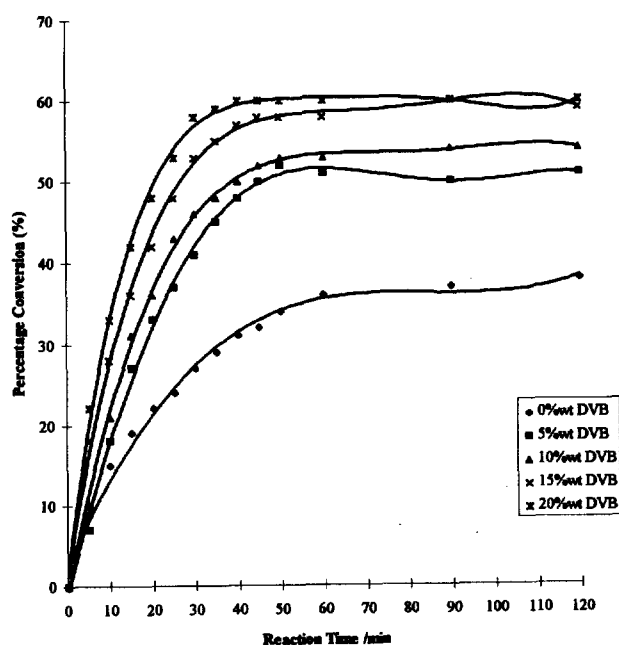

Fig. 7. Plot of hole mobility versus the square root of the applied field F measured by TOF for a polycarbonate CTL with 40% w/w of DEH.

Fig. 8. Percentage conversion with time (min) of styrene-co-DVB formulations with (◆) 0%, (■) 5%, (▲) 10%, (×) 155 and (×) 20% w/w DVB on thermally curing at 80°C (0.1% w/w AIBN).
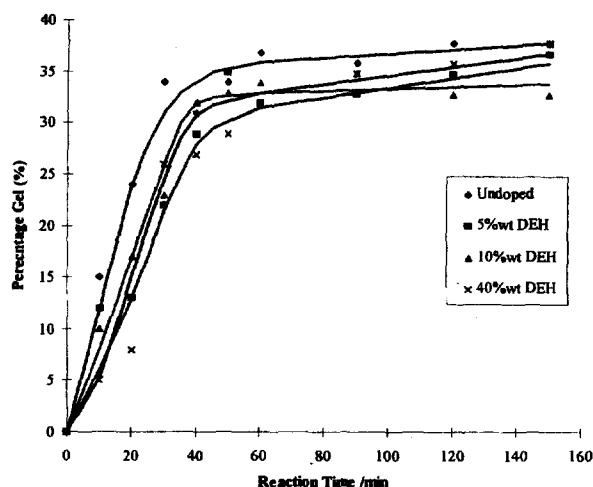
Fig. 9. Percentage gel vs. time of cure at 80°C for a styrene-co-DVB (10% w/w) mixture containing (♦) 0, (■) 5, (▲) 10 and (×) 40% w/w of DEH.
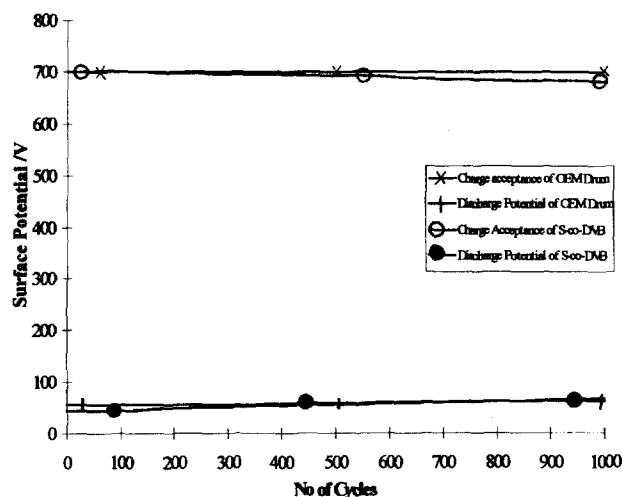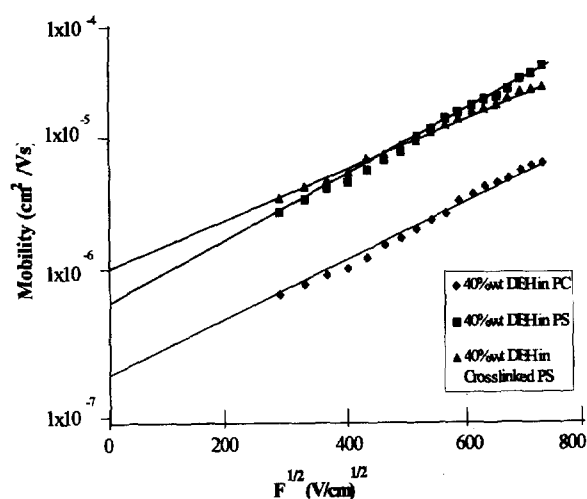

Fig. 11. Plot of hole mobility vs. the square root of the applied field F measured by TOF for a (♦) polycarbonate, (■) polystyrene and (▲) cross-linked styrene-co-DVB (10% w/w) with 40% w/w of DEH CTL.

Fig. 10. Surface potential before and after photodischarge vs. number of cycles of operation for a (×,+) commercial OEM drum and a (○,●) cross-linked styrene-co-DVB (10% w/w) CTL system.
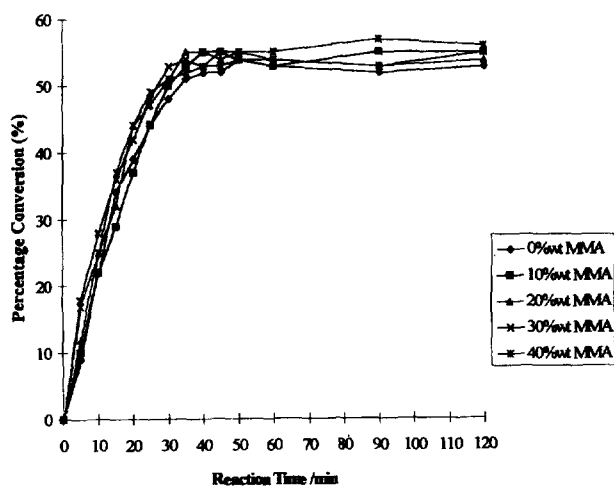

Fig. 12. Percentage conversion with time (min) of a styrene-co-DVB (10% w/w) mixture with (♦) 0%, (■) 10%, (▲) 20%, (×) 30% and (*) 40% w/w of MMA on thermally curing at 80°C (0.1% w/w AIBN).

throughout the study giving a total gel content after complete cure of 40% w/w of the coating. The presence of the CTM was also found not to influence significantly the rate of cure of the styrene-co-DVB system. This effect is shown in Fig. 9 for different concentrations of DEH on gel formation.

Charge-transport measurements were undertaken on both polystyrene and cross-linked styrene-co-DVB (10% w/w) systems doped with 40% w/w of DEH as the CTM. It is seen that an effective photoresponse is observed for both CTLs with a very slight increase in residual potential for the latter system. In comparison with the commercial OEM drum the cross-linked CTL was comparable in photoresponse. Polystyrene itself is known to be a highly effective photoreceptor binder [2,3] but fails on its mechanical durability. Charge transport measurements were performed to examine the long-term effects of fatigue on photoresponse. The results are shown in Figs. 10 and 11. Over 1000 cycles both the charge

acceptance and residual discharge potentials were comparable. The cross-linked system did display a very slight reduction in surface potential after 500 cycles but this is possibly associated with the absence of a blocking layer in the experimental CTL which would otherwise improve the charge. TOF experiments on hole mobility were interesting and are shown in Fig. 12. These show that the polystyrene exhibits higher hole mobility than the polycarbonate system [2,3]. The phenyl side groups in polystyrene are involved in stabilisation of the radical cations. The cross-linked polystyrene exhibits a slightly reduced mobility from that of polystyrene but nevertheless superior to that of the polycarbonate CTL. Polycarbonate is a more polar matrix and this can cause some charge trapping [2,3].

3.2.2. Styrene-co-DVB-co-MMA

The addition of MMA comonomer to the above styrene-co-DVB was found to increase the pendulum hardness of the
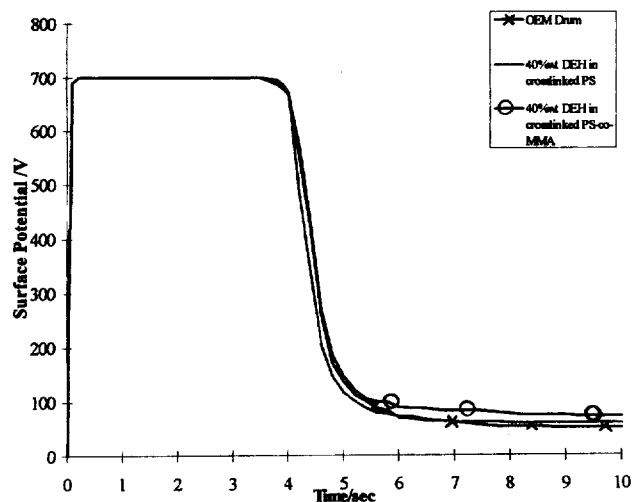
Fig. 13. Charge-transport showing surface potential (− ve) with time of a (−×−) commercial OEM drum, (————) cross-linked polystyrene and (−O−) thermally cross-linked styrene-co-DVB (10% w/w)-co-MMA (30% w/w) CTL with 40% w/w of DEH.
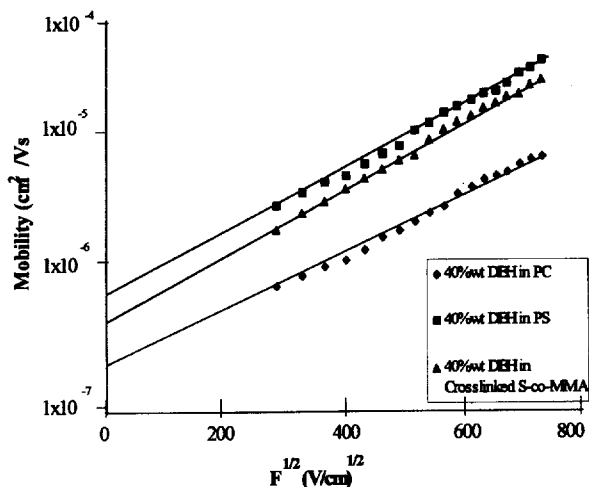

Fig. 14. Plot of hole mobility vs. the square root of the applied field F measured by TOF for a (♦) polycarbonate, (■) polystyrene and (▲) thermally cross-linked styrene-co-DVB (10% w/w)-co-MMA (30% w/w) CTL with 40% w/w of DEH.

cross-linked coating CTL. At 30% w/w MMA the oscillations increased to a value of 205 from 180 (Table 3). However, the addition of MMA monomer was found not to influence the rate of conversion of the system as shown in Fig. 13. The pendulum hardness was found to be a maximum at 30% w/w of MMA. Also, the presence of the CTMs were found to have no effect on the conversion rate/gelation of the styrene-co-DVB-MMA terpolymer.

The charge-transport characteristics of the styrene-co-DVB (10% w/w)-co-MMA (30% w/w) CTL are compared in Fig. 14 with those for the Styrene-co-DVB and commercial OEM drum. Rapid photodischarge was observed again showing that charge-transport is effective. There was a small residual voltage after discharge. TOF measurements are shown in Fig. 15 to measure the hole mobility. The cross-linked ter-
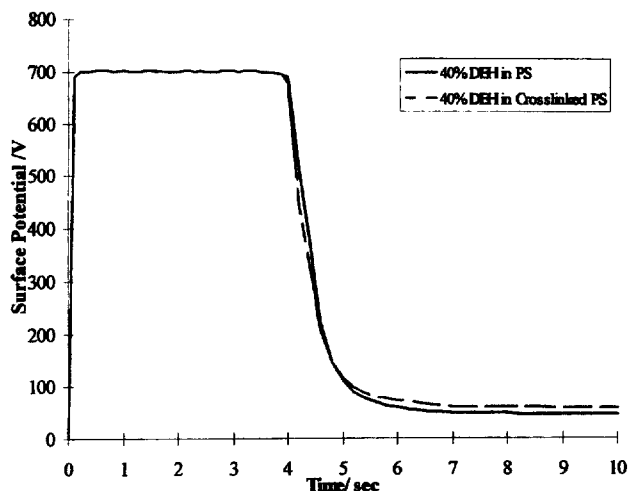

Fig. 15. Charge-transport showing surface potential (− ve) with time of a (————) polystyrene and (- - -) thermally cross-linked styrene-co-DVB (10% w/w) CTL with 40% w/w of DEH.

polymer was found to transport holes more effectively than the polycarbonate CTL but was less effective than the styrene-co-DVB copolymer. The latter effect may be associated with the increased aliphatic content of the network reducing interactions between the phenyl rings.

3.2.3. Styrene-co-Allyl methacrylate (AMA)

Attempts were made to produce a cross-linked styrene-co-AMA CTL via a two step curing reaction. Both UV and thermal induced reactions were successful with higher conversion for the latter. Under UV irradiation the allyl group is very unreactive. However, the major problem was the fact that the conversion was markedly inhibited by the presence of the CTMs. Despite this set-back cured CTLs could be made after drying the films in an oven at 80°C for 1 h using 20% w/w of AMA. Films made with all four CTMs exhibited effective discharge as found for polystyrene itself (see Fig.
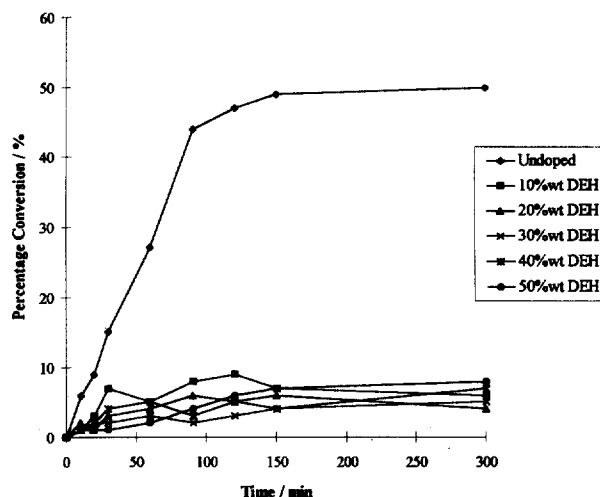

Fig. 16. Percentage conversion with time (min) of a styrene-co-AMA (20% w/w) mixture with (♦) 0%, (■) 10%, (▲) 20%, (×) 30%, (*) 40% and (●) 50% w/w of AMA on thermally curing at 80°C (0.1% w/w AIBN).
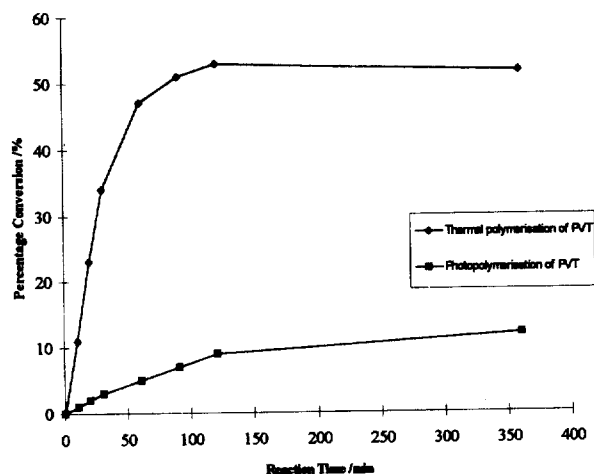
Fig. 17. Percentage conversion with time (min) of allyl cinnamate by (■) UV 400 W Hg and (♦) thermally curing at 80°C (0.1% w/w AIBN).
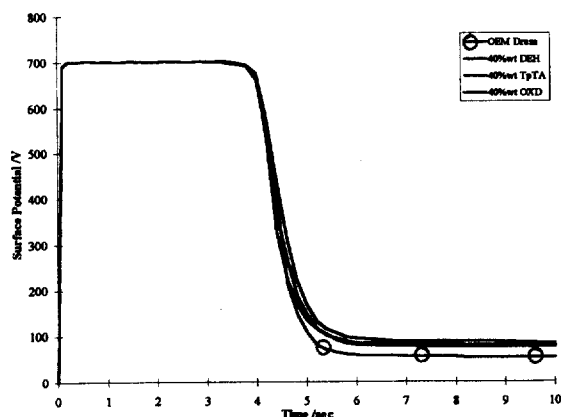

Fig. 18. Charge-transport showing surface potential (−ve) with time of a (–O–) commercial OEM drum, and (———) thermally cross-linked polyallyl cinnamate CTLs with 40% w/w of DEH, TpTA and OXD.

10). However, TOF measurements indicated that hole transport was reduced to that of polycarbonate itself (see Fig. 15).

3.2.4. Poly(allyl cinnamate)

This particular monomer is interesting since it will cure via two distinct mechanisms. The reactivities of the allyl and cinnamate groups are markedly different. The former tend to be unreactive in UV light while the latter will undergo a rapid 2 + 2 cycloaddition reaction to form a substituted cyclobutane ring structure. Thermal and photoconversions of the allyl cinnamate monomer are compared in Figs. 16 and 17. It is seen that thermal curing is more rapid and effective than UV curing. The presence of the CTMs also did not influence either of these processes at and up to 40% w/w addition. In terms of the photoreceptor characteristics the poly(vinyl cinnmate) gave hard CTLs after curing with a pendulum hardness of

270 (Table 3). Rapid discharge of the surface voltage was observed on irradiation using the electrophotographic system as shown in Fig. 18 for three of the CTMs studied, OXD, TpTA and DEH. TOF indicated hole transport as effective as polycarbonate.

4. Conclusions

The use of UV curing methodologies failed to produce effective photoreceptor CTLs on a number of accounts.
1. The polar nature of many of the functionalities.
2. The screening effect by the high levels of CTM.
3. The photolytic instability of the CTMs.
4. The formation of residual initiator/impurity traps.
5. Insolubility problems of some CTMs.

The preparation of styrene copolymer systems was more promising in terms of photoreceptor characteristics. Hard cross-linked networks produced with DVB exhibited excellent charge-transport and hole mobility superior to that of commercial polycarbonate systems. Some brittle features were still evident although these could be overcome by control of the comonomer ratio. Dual reactivity systems, whilst also effective can give rise to problems in terms of rates of total conversion. However, it is evident that careful design of copolymer systems is feasible for producing durable photoreceptor CTLs.

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