Photoreceptor Defects, Surface Hardness and Image Quality

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Abstract

Photoreceptor is a central device in digital printers. The outer layer, Charge Transport Layer made up of polycarbonate and Charge Transport Molecule is prone to abrasion by stresses of developing system or cleaning system when it is repeatedly used in printing process. The abrasion of the photoreceptor causes deterioration of electrical properties such as lowering sensitivity or lower charging and results in irregular image such as lower image density and image stain. Single and multiple coating were made with filled and unfilled binder polymers and their modulus and hardness were measured by nano-indenter. Charge Transport Molecule reduced modulus and hardness thus increasing photoreceptor wear rate. Nano-filler silica in the polymer either polycarbonate or polyester increased modulus and hardness with higher photoreceptor life.

INTRODUCTION

Photoreceptor is made up of multi-layered coatings which are applied either as a dip coating in drums or as a web coating for belts. Photogeneration of charge carriers (electron hole pairs) takes place in a thin charge generation layer (CGL), typically 0.5 pm thick, which is coated on a conductive substrate such as an aluminum drum. After photogeneration, mobile carriers (usually holes) are injected into a thicker charge transport layer (CTL), which is about 21 micron thick and coated on top of the CGL, under an electric field gradient provided by a negative surface charge. These holes drift to the outermost layer of the photoreceptor to selectively neutralize surface charger thereby forming a latent electrostatic image, which is subsequently developed by thermoplastic toner [1].

The physical durability of the organic photoconductive imaging receptor is the major characteristic that determines service lifetime, and such durability depends on the mechanical properties of the surface CTL. The CTL is formulated from two major components. They are electron donor molecules responsible for hole transport, known as the charge-transport material (CTM), and an appropriate binder resin, which must be amorphous and transparent to light. The CTM is usually a low molecular weight organic compound with arylarnine or hydrazone groups, and it is selected primarily on the basis of solubility, compatibility with the binder resin, charge transport property, and elec trophotographic cyclic stability. The CTM is a non-reactive binder resin diluent (molecular dopant), and it must be several type of abrasion mechanisms, but cyclic fatigue is the major factor. This may be reduced by absorption and dissipation of compatible in approximately equal parts by weight with the binder resin to ensure good charge mobility, which involves electron hopping between adjacent molecules of the CTM. Polycarbonates (PCR) have characteristics as solubility (to allow coating from solution), high carrier mobility, compatibility with the CTM, transparency, durability and adhesion to the CGL. The simplest and best known example is bisphenol-A polycarbonate (BPA-PCR), This binder polymer has poor stability in solution, has a tendency to stress crack and phase separate from the charge transport material in the solid state, leading to an opaque charge transport layer with unacceptable performance. It is not resistant to surface scratching and abrasion caused by physical contact of the surface of the CTL with paper and machine components designed for the addition and removal of toner.

Abrasion of polymers is a complex phenomenon, involving both surface and bulk properties. Generally, at least two basic kinds of abrasion mechanism are involved: scratch (penetration and plowing of the polymer matrix by a hard asperity); and fatigue (gradual loss of the entire surface layer by repetitive cyclic loading under adhesive contact). Under the actual service conditions of organic photoconductive imaging receptors, there are contributions from external stress as internal heat, which can quickly and harmlessly diffuse through the thin CTL into the aluminum substrate, provided there is efficient coupling to a mechanical loss process at the temperature of operation. Otherwise, mechanical stress remains concentrated at the surface, with the likelihood of increased abrasion. The resistance of a CTL to mechanical fatigue by cyclic stress correlates with the temperature profile of the dynamic ‘mechanical loss modulus. Two mechanical loss peaks are of significance: l) the primary relaxation (α peak), which occurs at a higher temperature and results from long-range segmental motion at the glass- transition temperature, Tg; and 2) the secondary sub-T3relaxation (γ peak), which occurs at lower temperature.

Wear is quantitatively measured in terms of the mass, or volume, loss from a sliding or eroding contact. The scaling approach of wear is a two-term non-interacting model of friction. Friction is, as a first approximation, of two kinds: interfacial and bulk friction. Frictional work causes the damage and the subsequent wear, wear is classified as `cohesive’ and `interfacial’ in its nature. Another approach of treating polymer wear is phenomenological and considers wear processes by abrasion, transfer wear, fretting, chemical wear, erosion, fatigue wear, and delamination wear. The third approach recognizes the extremely wide diversity of response of polymeric systems and focuses upon the material response combined with the prevailing contact deformation. Thus, wear can be subdivided according to material response to produce a scheme where each polymer class is dealt with in relative isolation from the rest. In this type of division elastomers, thermosets, glassy polymers and semi-crystalline polymers can be distinguished as having unique attributes in the context of their wear behavior [2].

The methods for improving abrasion resistance of the photosensitive layer includes (1) applying an overcoat on the transport layer (2) substituting for a stronger polymer binder in the charge transport material (3) the sol- gel binder in the surface layer,(4) having inorganic filler (nano filler)dispersed in the binder

(5)putting lubricant in the transport layer for reducing friction with the cleaner. Abrasion of polymers is a complex phenomenon, involveing both surface and bulk properties.

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In plowing or abrasive wear, subsurface damage in material can be caused by surface sliding in two ways. First, if a polymer is sliding against a rough and hard surface, the asperities of the hard surface can plow into the bulk of the polymer removing debris. These debris materials generally get transferred to the counter face, forming a transfer film (also known as the “third body”), which eventually makes the counter face appear smoother. The formation of a stable film at the counter face leads to a change in the wear rate of the polymer. The second cause of subsurface damage is through subsurface fatigue cracks, which can lead to the removal of material when these cracks grow to the surface of the polymer. Fatigue wear removes the material in chunks or flakes.

The most notable model for wear where elastic-plastic contact occurs, wear volume is given by Ratner-Lancaster. The relation is given as:

$$V = \frac{K\mu W v}{HS\varepsilon} \qquad (1)$$

where V is the wear volume, K is a proportionality constant also termed wear rate, v is the sliding speed, μ is the coefficient of friction, H is the indentation hardness, S is the ultimate tensile

strength, and ε is the elongation to break of the polymer. Another wear model, Kar and Bahadur obtained a relation given as

$$\mathrm{V} = \frac{1.5K\gamma^{1.775}p^{1.47}Z^{1.25}}{E^{3.225}} \qquad (2)$$

where c is the surface energy, Z is the sliding distance, and E the modulus of elasticity of the polymer[4].

The extent of the reinforcing effect depends on the properties of composite components, and it is strongly affected by the microstructure represented by the filler size, shape, homogeneity of distribution/dispersion of the particles within the polymer, and filler/matrix interface extension. This latter plays a critical role, since the composite material derives from a combination of properties, which cannot be achieved by either the components alone. Thus it is generally expected that the characteristics of a polymer, added of a certain volume fraction of particles having a certain specific surface area, are very strongly influenced when very small particles (*nano fillers*), promoting an increased interface within the bulk polymer, are used [5].

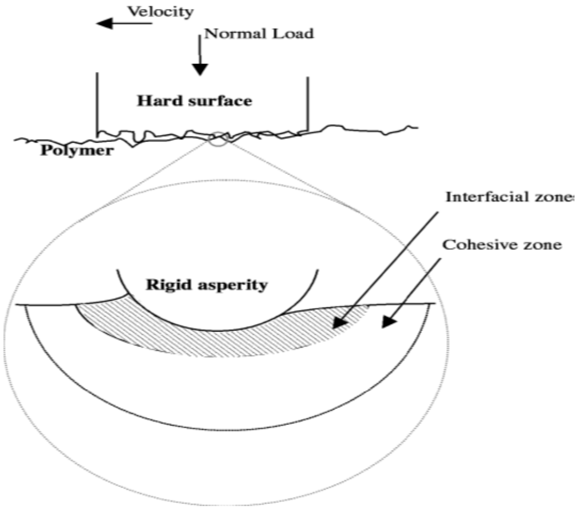

Figure 1 *Two-term model of the wear processes. The distinction between interfacial and cohesive wear processes from the extent of deformation in the softer material (usually polymer) by a rigid, non -dissipative, asper ity of the counter face. For interfacial wear the frictional energy is dissipated mainly by adhesive interact ions while for cohesive wear the energy is dissipated by adhesive and abrasive (subsurface) interactions*

Nano fillers usually tend to aggregate because of their high specific surface area, due the adhesive interactions derived from the surface energy of the material. In particular, the smaller the size of the nanoparticles, the more difficult the breaking down of such agglomerates appears, so that their homogeneous distribution within the polymer matrix is compromised.

Compared with previous works which focus on bulk properties, indentation modulus and hardness of polymer films are determined and used to predict photoreceptor properties for digital images.

There are some inherent advantages in processing nanomaterials via high-energy ball milling techniques,such as excellent versatility, scalability, and costeffectiveness Therefore high-energy ball milling techniques are well suited for manufacturing largquantity of nanomaterials.

Polycarbonate Makrolon of molecular weight of 80,000 and molecular distribution of 2.2 was dispersed in the presence of toluene with nano-particles of silica at different concentrations in a high speed mixer and spray coated on the surfaces of aluminum plates.. The spray coatings were dried and the dried coatings were subjected to nanoindentation using a nanoindenter made by Hysitron. Contact area was calibrated by using silica and polycarbonate of known modulus and hardness. The applied load P and the indenter displacement h are logged continuously with respect to time t. The tip-sample contact stiffness S is evaluated from the onset of unloading from the peak load, and then the contact area Ac is evaluated from S. The reduced modulus is calculated using the following equation where S is the contact stiffness and Ac the contact area under load. In nano-indentation, the contact area is obtained via a pre- calibrated shape function of the tip.

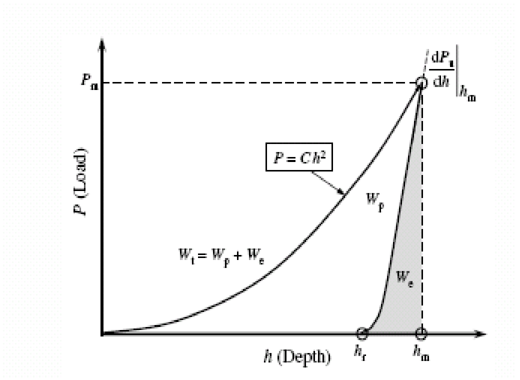

Figure 2 *Load indentation depth curve*

$$h_c = h_m - \gamma P_m / \left.\frac{dP_u}{dh}\right|_{h_m} \tag{3}$$

$$A_m = \pi a_m^2 = \pi h_c^2 \tan^2\theta \tag{4}$$

$$E^* = \frac{1}{\beta}\left.\frac{dP}{dh}\right|_{hm} \frac{1}{2}\frac{\sqrt{\pi}}{\sqrt{A_m}} \tag{5}$$

$$E^* = \left[\frac{1-v^2}{E} + \frac{1-v_i^2}{E_i}\right]^{-1} \tag{6}$$

where β is a correction factor , E* is the reduced modulus, E are the Young's modulus and the Poisson ratio, h is the contact depth. Here dP/dh can be evaluated via a power law fitting function of the unloading curve or the continuous stiffness measurement (CSM), in which a number of partial unloading steps are superimposed on the loading curve can be evaluated via a power law fitting function of the unloading curve or the continuous stiffness measurement (CSM), in which a number of partial unloading steps are superimposed on the loading curve

Requirements
1) Careful calibration of the machine compliance
2) Identification of the first indenter–surface contact point
3) Determination of the area function.

Issues
1) The method does not rigorously account for pile-up (or sink-in)
2) The value of the correction factor β used. For a Berkovich indenter, the commonly used values in the available literature are between 1.034 and 1.09. An accepted consensus on β requires thorough three-dimensional (3-D) computational investigations.

The materials used in our study are given in Table 1. They show significant differences in molecular weight (Mw), .in glass transition and in chemical structure. Compared to Polycarbonate (PC-A), Polyester has lower Mw but lower Tg. Polyvinyl Butyral has higher molecular weight but lower Tg than the polyester. Hardness decreases with increase with the depth of indentation irrespective of the polymer.

The two layers PC/PE shows higher hardness than PC alone at shorter depth of indentation and as the depth of indentation increases difference in hardness narrows and at 800nm, hardness of PC/PE is lower than that of PC. This behavior can be explained by the compatibility of polycarbonate with polyester. Compatibility between two polymers indicated by the presence of a single Tg on mixing leads to increase in resistance to deformation. Polyester PE-100 compared to PC has both lower Mw and lower Tg gives a significantly steeper slope with increasing depth of indentation. Polyester chains are in likelihood more flexible and less entangled.

They offer very little resistance to deformation. Polyvinyl butyral compared to polyester has lower Tg but higher molecular weight. At shallower depth of indentation, effect of Tg on hardness seems to dominate. At higher depth of indentation, molecular weight is dominant. The effect of depth of indentation on modulus is different from that on hardness particularly on comparing PC/PE to PC. Throughout the range of indentation, modulus of PC/PE is higher than that of PC and does not go through crossover. Elastic effects dominate compared to hardness where elastic plastic deformation is reflected.

The elastic modulus of nano-composites of polycarbonate filled with silica increases to 5% level but then decreases as the concentration of nano-filler is increased to 10% level.

Elastic modulus at 10% level is lower than the elastic modulus at 3%level.

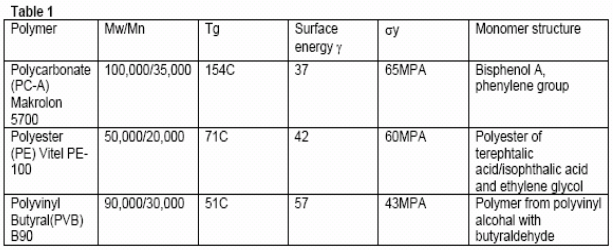

Table 1

Polymer	Mw/Mn	Tg	Surface energy γ	σy	Monomer structure
Polycarbonate (PC-A) Makrolon 5700	100,000/35,000	154C	37	65MPA	Bisphenol A, phenylene group
Polyester (PE) Vitel PE-100	50,000/20,000	71C	42	60MPA	Polyester of terephtalic acid/isophthalic acid and ethylene glycol
Polyvinyl Butyral(PVB) B90	90,000/30,000	51C	57	43MPA	Polymer from polyvinyl alcohal with butyraldehyde

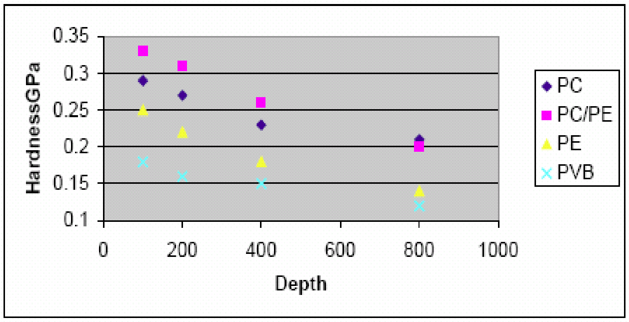

Figure 3 *Hardness dependence on depth for various binder polymers*

Table 2 Effect of surface hardness of PC Diamine composite on depth

Depth (nm)	PC (GPa)	PC +10% Diamine GPa	PC +20% Diamine (GPa)	PC +40% Diamine (GPa)
100	0.34	0.31	0.27	0.25
200	0.30	0.28	0.25	0.23
400	0.26	0.24	0.21	0.19
800	0.23	0.22	0.18	0.17

The properties of composite materials, such as elastic modulus of the composites depend on component moduli, size, shape and arrangement of inclusions, and matrix inclusion interface. The effects of the nanoparticles on composite modulus are dependent on many variables particularly on the morphology of the polymer matrix as well as the interaction between the filler and matrix. As the concentration of filler increases it becomes difficult to disperse the filler homogenously in the polymer matrix Polymer- filler interaction depend on wettability and adhesion of the filler to the polymer matrix. If the wettability of the filler to the polymer surface is poor, voids are created around the filler causing structure to slip under stress thus lowering tensile modulus.

The state of dispersion depends on balance of repulsive and attractive forces. on the particles. There are four interaction forces to consider long range repulsive electrostatic forces, short range attractive van der Wall forces, attractive depletion forces and repulsive steric forces.

Similar to elastic modulus, hardness of nano-composites of polycarbonate also increases as silica nano-filler concentration is increased up to a threshold level beyond which the hardness drops dues to aggregation of nanofillers and their adhesion to the polycarbonate matrix.

This behavior of polycarbonate with charge transport molecule fits with the conventional concept of antiplasticization, which has been described for other low molecular weight diluents in PC(6). Antiplasticizer effect is shown when an organic molecule, a diluent is added to polycarbonate resulting in lowering of Tg, increase in modulus and reducing strain to break. The effect of hard filler such as silica in polycarbonate is affected by polymer silica interface which at high loadings can undergo slippage and debonding. Thus addition of 5% level of nano filler silica would reduce wear life of photoreceptor, reduce likelihood of early irregularity of image and enhance printer life.

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Author Biography

After finishing Ph. D in polymers at the Polytechnic Institute of New York, Suresh(Sam) Ahuja worked as a scientist and Project Leader at Keuffel and Esser on effect of crystallinity and orientation of polymer films on non-silver halide imaging system collaborating with Rutger University and Union Carbide (Jim White). He has over thirty eight years of experience at Xerox Corporation as Principal Scientist and a Project Manager of a team of scientists. He has been a task Leader for over thirty task forces. He is responsible for over hundred papers and over 20 US and European patents. He has coordinated digital imaging activities with academicians from University of Massachusetts, University of Karlsruhe, Rensselaer Polytechnic Institute (RPI), University of Rochester, University of Cornell and University of Minnesota, He has given seminars at various universities and has been a continuing education instructor for teaching structure and rheology of polymers, as well as, for teaching elasticity, plasticity and viscoelasticity in polymers. His research activities has concentrated on analysis of melt processes in composites using roll milling, on-line extrusion, as well as, analysis of film coatings using dip coating and slot coating. His particular interests comprise review of liquid crystal polymers, nano-indentation of multi-layered coatings, sintering and fracture/yielding behavior of nano size particles and their aggregates