# Toner Photoreceptor Adhesion and Crosslinked Polyamide Material

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#### **Abstract**

The adhesion of two different solid surfaces can be predicted from their ability to induce spontaneous spreading of high surface tension liquids, because interfacial forces govern both the processes. The friction behavior of solid surfaces, on the other hand, is controlled by the interfacial dynamics, which has some features that are common to the sliding behavior of a liquid drop on a solid surface.

Our work consisted of making polyamide and acid cured polyamides coatings. They were indented at different depths using a nanoindenter. It is well known that strain softening and strain hardening are analyzed by the effect of modulus and hardness on depth. Elastic plastic model has been used to analyze strain softening or strain hardening. Glass transition and molecular weight are important variables that affect strain dependence on modulus and hardness. In the polyamides and cross-linking polyamides, strain hardening is shown along with significant increase in modulus reduction in coefficient of friction. The results are applied to models of adhesion between toner and photoreceptor and it is shown that experimental results are consistent with the model predictions.

# Introduction

Photoreceptor belts or drums used in copiers and printers contain Charge Transport layer with polycarbonate and diamine molecule, a charge transport small molecule. Charge transport molecule makes polycarbonate less flexible and reduces the strain at which the composite fails in brittle fashion. In order to increase photoreceptor life, cross-linked polymers and nano-composites are proposed to be used in conjunction with polycarbonate diamine composite. Recently there have been patents regarding the effect of concentration of diamine [1], addition of silica [2] or addition of overcoat [3] on photoreceptor properties.

The patent on cross-linked polyamide overcoat uses an electro-photographic imaging member consisting of a photoconductive layer and a partially electrically conductive overcoat layer comprising finely divided charge injection enabling particles dispersed in a charge transporting continuous matrix comprising a cross linked polyamide, charge transport molecules and oxidized charge transport molecules, the continuous matrix being formed from a solution selected from the group consisting of a first solution comprising cross-linkable alcohol soluble polyamide containing methoxy methyl groups attached to amide nitrogen atoms, an acid having a pK.sub.a of less than about 3 with examples of oxalic acid, picric acid etc.

Nanoindentation of polymer layers have been used to investigate strain softening and strain hardening. In strain softening, elastic modulus and hardness decrease with the depth of indentation, where as, both elastic modulus and hardness increase with depth. Effect of cross-linking is to increase weight average molecular weight and entanglements. As the molecular weight increases, dynamic elastic modulus increases in a higher power exponent than does viscous modulus. Tan delta being the ratio of viscous modulus to elastic modulus and a bulk friction parameter decreases with increase in molecular weight and polymer chain. entanglements.

## **Method and Materials**

Polyamides were cross-linked at different gel levels. The solution coatings on the aluminum surface were dried at 130C and subjected to indentation using a Hysitron nanoindenter.

#### **Results and Discussion**

Charge Transport layer consists of polycarbonate and diamine molecule, a charge transport small molecule. The effect of diamine molecule in polycarbonate is to decrease Tg of the polycarbonate composite, decrease percentage of strain to break and increase Young's modulus (see Table 1 and Figure 1). The additive in the polycarbonate acts as an anti-plasticizer. The degree of the anti-plasticizing effect, polymer, depends on the type and level of the additives used. It is considered that for an additive to act as an antiplasticizer its molecules should be compatible with the polymer, relatively planar and rigid, and contain such atoms as halogen, nitrogen, oxygen, etc. The majority of known antiplasticizers are low molecular weight substances and most studies of anti-plasticization have been devoted to the polymer-diluent interaction [4]. Antiplasticization was found in Polycaprolactone PCL/ PC modified epoxy system, cured with Diamino Diphenyl Methane DDM. The initial modulus increased and the fracture toughness and the elongation at break decreased with the addition of the PCL/PC (1/10) modifier up to 15 phr. The glass transition temperature (Tg) slightly decreased. The antiplasticization phenomenon can be explained by the formation of hydrogen bonding between the carbonyl groups in the PCL/PC and the hydroxyl groups in the epoxy. The hydrogen bonding proportion, as analyzed from Fourier transform infrared spectra, increased with the addition of PCL/PC (1/10) up to 15 phr. It is suggested that for anti-plasticization to occur within the miscibility range, a strong molecular interaction is necessary to restrict molecular motion, and in turn to decrease the free volume. Dynamic mechanical analysis revealed an increase in the activation energy and a decrease in the peak area for the beta relaxation process, which also can be explained by the hydrogen bonding. The results indirectly support the hypothesis that the

motion of the 2-hydroxypropyl-ether moiety is responsible for the beta relaxation process [5,6].

Table 1 Properties of polycarbonate containing various
concentrations of diamine

Concentrations of diamine					
Proper	0%	10%	20%	40%	
ty	Diamine	Diamine	Diamine	Diamine	
Tg©	150	120	100	80	
%	50	30	20	5	
Strain					
to break					
E	400	420	450	500	
(Mpa)					
	3.5	2.1	1.4	0.35	
Toughness (Mpa/m)					

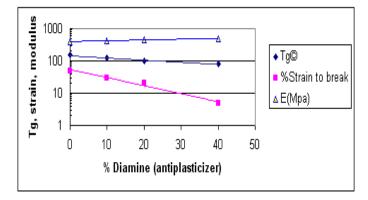


Figure 1 shows the Effect of% Diamine in PC

Tests of adhesion are essentially fracture tests and, like the cohesive or bulk fracture of a material, they require an understanding of the mechanics that occurs close to the crack tip and of the material deformations caused by this mechanical situation. In fracture mechanics tests, the results are given as either Gc, the critical value of G, the strain energy release rate (or fracture toughness), or Kc, the critical stress intensity factor. Since Gc is a measure of the energy dissipated per unit crack area formed, it has units of surface energy. Numerically, it is normally orders of magnitude larger than both thermodynamic surface energies and the energies necessary to break chemical bonds and form a new surface in a polymer. The vast majority of the energy that G, measures goes into the necessary plastic or viscous processes that occur round a crack tip in loading the actual tip to the breaking point. In adhesion interfaces between two different materials is of great significance. Interfacial strength and toughness increases with increase in interfacial width. Review of several models indicates that interfacial width is inversely proportional to  $\mathcal{X}$ , Flory-Huggins interaction parameter. Previous work on both  $\mathcal{X}$  and the interfacial toughness between polycarbonate (PC) and a series of styrene-acrylonitrile copolymers showed that  $\mathcal X$  went through a minimum and the interfacial toughness went through a maximum at a copolymer

composition of about 23% by weight of acrylonitrile. [7]. In most cases however, the contact deformations obtained from the loading and unloading cycles exhibit hysteresis, which are sensitive to the structure and chemical compositions of the interfaces. Nanoindentation of the crosslinked polyamide coatings under dynamic deformation gave elastic modulus, viscous modulus and tan delta. Elastic modulus increased with depth of indentation much more the viscous modulus. Fracture of the majority of materials, such as polymers, involves many irreversible processes associated with macroscopic deformations that dissipate energy from the applied stress e.g., plastic yielding, acoustic emission, etc. The total fracture energy associated with the creation of two similar surfaces is given by.

$$G_c = G_0 + \psi \tag{1}$$

$$\psi = G_0 f(\dot{a}, T, \varepsilon) = W_p \tag{2}$$

 $G_0$  is the energy to propagate the crack along the interface in the absence of viscoelastic losses and  $\Psi$  is the viscoelastically dissipated energy dependent upon the crack rate,  $\dot{a}$ , temperature, T, and strain  $\epsilon$ 

For crosslinked polymers, the fracture involving 'v ' chains in the fracture plane is given as

$$G = vN_cU_c = \frac{U_c}{N_c^{1/2}a^2}$$

$$N = \frac{M_w}{m}$$
(3)

(4)

where "a" is the statistical size of the monomer segment,  $U_c$  is the energy required to break an individual covalent bond in the chain and  $N_c$  is the polymerisation index of the cross-linked polymer with the chain density, V, per surface of ideal fracture area [8]. Polymerization index is the ratio of  $M_W$  and m, molar mass of the monomer. The relationship between N and molecular weight  $M_W$  shows that as the polymerization index of the cross-linked polymer is increased, fracture energy increases.

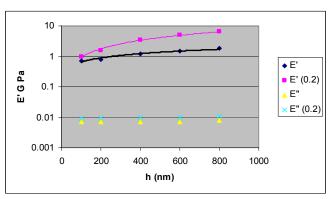


Figure 2 shows elastic modulus and viscous modulus of linear and 0.2% gel Crosslinked polyamide coating at different depths of indentation.

Adhesion of toner to the photoreceptor surface is dependent on interface between toner and the photoreceptor. In addition to properties of toner particles or aggregates, photoreceptor surface and its properties play a significant role in toner photoreceptor adhesion. For normal contact between a spherical toner particle and a flat photoreceptor surface radius of contact a is given by [9]

$$\frac{a^{3/2}}{R} = \left(\frac{1}{K}\right) \left(\frac{P}{a^{3/2}}\right) + \left(\frac{6\pi W}{K}\right)^{1/2}$$

(5)

where W is the work of adhesion, R is the toner radius, P is the normal load. K is given by

$$K = \frac{4E^*}{3}$$

(6)

$$\frac{1}{E^*} = \frac{\left(1 - {\nu_1}^2\right)}{E_1} + \frac{\left(1 - {\nu_2}^2\right)}{E_2}$$

(7)

where V is the Poisson ratio of toner and photoreceptor and E is the elastic modulus for toner(1) and photoreceptor(2). Crosslinking of polyamide on photoreceptor surface increases its elastic modulus that should decrease contact radius with toner and thereby decrease work of adhesion. During cleaning of photoreceptor, shear forces on toner in contact with photoreceptor, results in toner either moving smoothly or in stick-slip fashion, Studies have indicated that adhesion hysteresis and friction, two types of energy dissipative processes occurring at interfaces, are related. Increase in cross-linking of polyamide is shown to result in decrease in the ratio of  $\tan \delta$ , ratio of viscous to elastic modulus. A review of solid friction shows that it is made up of surface roughness, surface energy and Tan  $\delta$  [10]. Decrease in

Tan  $\delta$  on cross-linking of polyamide would result in reducing toner photoreceptor adhesion.

## Conclusion

Polycarbonate is a flexible and tough polymer but on addition of Charge Transport Small Molecule to polycarbonate resulted in increase in brittleness and decrease in toughness. Coss-linked polyamide overcoat increases elastic modulus and reduces friction. Its effect is to reduce wear and lengthen life of the photoreceptor.

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Suresh Ahuja received his BS in physics and chemistry from the Punjab University (1959), his MS in Soil Physics from Indian Research Institute (1961) and his PhD in Polymer Physics from Polytechnic Institute of Brooklyn (1967). After working over 37 years at Xerox for several years as Principal Scientist, he retired. He has twenty patents. He has published over 40 publications and presentations at international conferences. He is a member of APS, ASME, SOR and IST.