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Effect of pigmentation on fracture toughness of paint films

S. K. SINGH, S. P. TAMBE, D. KUMAR
Naval Materials Research Laboratory, Shil-Badlapur Road, P.O. Anandnagar, Ambernath 421506, Thane, India
E-mail: dhiren@ncml.ernet.in

The ability of paint films to preserve their physical integrity and to protect substrate from environmental deterioration depends on their mechanical properties. Amongst these properties, resistance to propagation of an existing crack, a measure of fracture toughness, is of paramount importance. The presence of a crack in the paint can be either due to a film defect occurring during application or mechanical damage or weathering during service. A poorly designed paint composition may also develop cracks due to high stress concentrations when applied over edges and sharp corners. In multiple coat systems, cracking can occur if individual coats do not match in mechanical properties. Such cracks may extend due to slow cycles of deformation over a period and expose the substrate to the environment.

Mechanical properties, such as tensile strength, flexibility, impact strength, abrasion resistance etc. are influenced by the nature and concentration of polymeric systems and of pigments in the paint formulations. While polymeric systems are suitably modified by incorporation of flexible resins and plasticizers, pigments enhance rigidity of paint films, which could influence crack propagation in dried coating.

A paint composition is essentially a homogeneous dispersion of pigments/extenders in a liquid binder/solutions. After application, liquid paint dries to thin layers containing pigments/extenders and binder. Hence, coating materials can be considered analogues to particulate filled composites [1], which are produced by dispersion of inert fillers in suitable resin systems. Composites are generally used in the form of thick block/sheets/rods with dimensions more than 6 mm. In contrast, paint films have thicknesses below 250 microns, however, they are always supported on a substrate. Mechanical properties including fracture toughness characteristics of composites are influenced by shape, size and concentration of pigments and extenders. A number of publications dealing with such parameters are available in literature [2–13].

Resistance to crack propagation, which is measure of fracture toughness, is influenced by volume fraction of fillers in a composite system. Theocaris *et al.* [2] have observed that at filler concentrations greater than optimum value, the continuity of the binder network is disturbed which leads to deterioration rather than improvement in mechanical properties as well as reduced resistance to crack propagation. Ahmed *et al.* [7] have reported that increasing volume fraction of rigid particles after a certain fraction decreases fracture surface energy of polymeric composites. They explained that effectiveness of pinning is a function of overlapping stresses associated with the crack front as it moves between the dispersed particles. Fracture toughness determination involves measurement of energy, when precracked sample is stressed in tensile mode. For viscoelastic materials such as filled polymer composites, crack propagation is analyzed using elastic-plastic fracture mechanism. The reasons for not using linear-elastic fracture mechanics for determination of fracture toughness of polymeric materials have been discussed by Hashemi *et al.* [14]. Ryntz *et al.* [15] have used an essential work of fracture method to correlate fracture toughness with scratch resistance of unpigmented coating. Literature [16, 17] on determination of fracture toughness of clear/unpigmented coatings are available, but we have not come across any reported work, where essential work of fracture method has been used to study the effect of pigments on fracture toughness of coatings. In the present work, the essential work of fracture has been determined for epoxy resin films containing rutile titanium dioxide pigment at six concentrations in the range 10 to 35%. Study was not carried out at 5% pigment volume concentration (PVC) because sufficient opacity could not be achieved at this concentration of titanium dioxide. The aim of this study was to determine the optimum pigment concentration for formulation of protective coatings with improved performance and reduced crack propagation characteristics.

Low molecular weight epoxy resin (M/s Ciba) and polysulphide modified epoxy resins (M/s Morsun Coatings) were used in the investigation. Modified polyamide resin (M/s Ciba) was used as curing agent for epoxy resin. Important characteristics of these resins are given in Table I. The pigment employed was titanium dioxide , R-902 grade of M/s Dupont. Xylene (IS: 359–1965) used in the paint formulation was of commercial grade. Its distillation range was 143–146 °C.

Epoxy resin blend comprising of epoxy resin and polysulphide modified epoxy resin as flexibilizer, at 25 phr, was used as binder for paint formulations. Titanium dioxide pigment was dispersed in binder at varying pigment volume concentrations (PVC), 10, 15, 20, 25, 30 and 35% in laboratory cavitation mixer. Requisite quantity of xylene was added during dispersion to obtain compositions with a solid content of 90 ± 2 percent by volume in mixed paint. Modified polyamide resin was used for curing of base compositions, at room temperature.

Free films of pigmented epoxy paints were prepared by casting films on glass plates precoated with carboxy methyl cellulose releasing agent using motorized film applicator blade, having clearance of 400 microns.

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TABLE I Characteristics of resins

Properties	Epoxy	Modified epoxy	Modified polyamide
Epoxy equivalent	190	380	–
Amine value, mg of KOH	–	–	224
Viscosity at 25 °C, poise	60	14	40
Volatile matter, weight percent	–	8.0	–

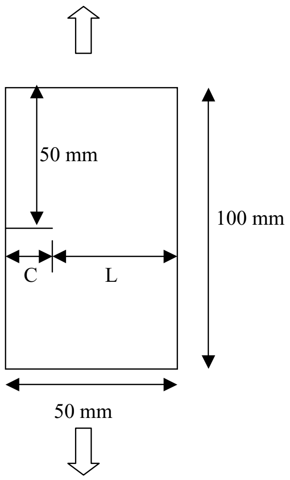


Figure 1 Details of film specimens used for fracture toughness studies.

Films were kept in dust free environment at ambient conditions. The films were removed carefully from glass plate after 48 h by peeling and washing under running water to remove methyl cellulose. The films were dried and conditioned for 48 h at 50% RH and employed for study of different properties after seven days of curing. Thickness of films was recorded using Elcometer digital thickness gauge.

The specific work of fracture, (W_f), of paint films were determined using single edge tension (SET) specimens of dimensions 100 mm × 50 mm. This size of specimen facilitated alignment in grips of 50 mm width with the axis of instrument. The crack length, C, varied from 5 to 25 mm as shown in Fig. 1. These cracks were prepared by slowly pushing the fresh edge of a razor blade into the material across thickness of the film. Crack length was accurately measured using a traveling microscope. During testing, the sample was fixed in such a way that precracked portion of specimen was situated at a distance of 12.5 mm from one of the pneumatic grips. Specimens were fractured on Universal Tensile Testing instrument (Instron 1123) and load—displacement curve for each specimen was recorded using a cross-head speed of 0.5 mm per minute. Before testing, specimens were conditioned for 48 h at 50% relative humidity.

The specific work of fracture, W_f, of specimens was obtained by calculating area under the load—displacement curve for each ligament length of the specimen. The data on specific work of fracture and ligament length produced a straight line (Fig. 2) as per Equation 1 proposed by Hashemi *et al.* [14]. The back extrapolation to intercept gives essential work required for fracture, W_e.

$$W_f = W_e + L\beta W_p \tag{1}$$

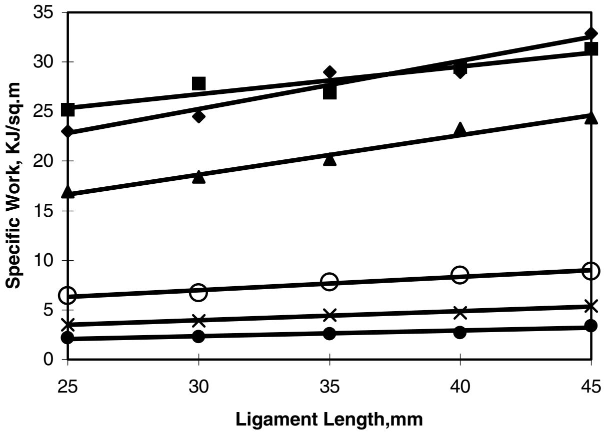


Figure 2 Determination of essential work of fracture (W_e) for titanium dioxide pigmented compositions at different PVCs using regression analysis: (■):10%; (♦): 15%; (▲): 20%; (○): 25%; (×): 30%; (●): 35%.

where W_p is the specific plastic work of fracture, L is the ligament length or uncracked width of specimen and β is a shape factor, which describes the size of plastic zone.

The details of Equation 1 are given by Hashemi *et al.* [14] who studied fracture behavior of thin films (0.1–0.265 mm thickness) of poly (ether-ether ketone). Typical graphical estimates of essential work of fracture, W_e, for the films of different titanium dioxide pigment contents, are given in Fig. 2.

Crack propagation in particulate filled composites has been explained by four mechanisms [7]: (a) filler particles diverting the crack and increasing the surface area, (b) absorption of energy due to deformation of filler, (c) increased plastic deformation of the matrix and (d) pinning of the crack causing the crack front to bow out between the particles. However, crack pinning has been found to be most likely mechanism [6, 7, 18–20] for increasing resistance to crack propagation.

It can be seen from Fig. 3 that essential work required for fracture increased with pigment concentration and maximum was achieved at 15% PVC of titanium dioxide. Scanning electron microscope (SEM) photographs of fractured surface of binder and pigmented titanium dioxide at two concentrations are shown in the Fig. 4. It is evident from the Fig. 4a that fractured surface of binder is smooth because there is no obstruction in the path of the crack and hence, the resistance to crack propagation is low. As the pigment is added, the pigment particles act as obstacle and the crack front is momentarily

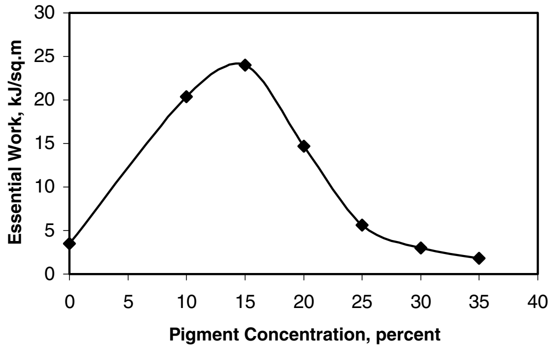
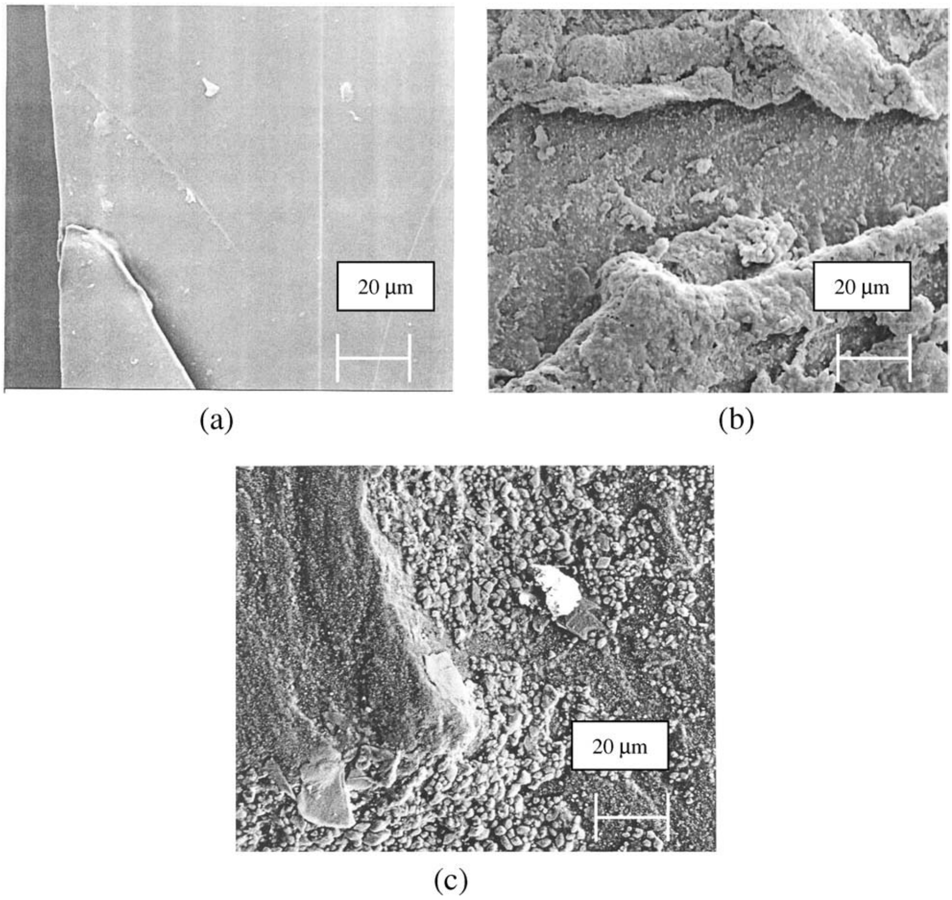


Figure 3 Essential work of fracture (W_e) for compositions pigmented with titanium dioxide.



(a) (b)

(c)

Figure 4 SEM photographs of fractured surface: (a) epoxy resin, (b) 15% PVC composition, and (c) 20% PVC composition.

pinned at the pigments. This interaction between pigment particle and crack front leads to bowing out of the crack front from the pinned position, thus, increasing its total length [7]. It can be seen from the SEM photograph of 15% PVC (Fig. 4b) composition that titanium dioxide particles are distributed throughout the matrix. Enhanced resistance to crack propagation at 15% PVC could be attributed to maximum crack pinning by optimum distribution of titanium dioxide particles in the matrix. Igakura *et al.* [21] have reported that particle distribution state in matrix has significant effect on fracture toughness of epoxy resin. It can be seen from the Fig. 4c that at 20% PVC, agglomeration of titanium dioxide particles has taken place due to its fine particle (0.3 μm) size. Due to agglomeration of titanium dioxide particles, the binder could not wet the pigment and consequently the crack moved easily through agglomerated pigment particles attached to each other by secondary valence forces. Increase in pigmentation beyond 20% PVC led to more severe agglomeration of titanium dioxide particle and further reduction in resistance to crack propagation was observed (Fig. 3).

In the present study it has been found that pigmentation of epoxy resin increases the resistance to crack propagation. The resistance to crack propagation increases to a maximum at 15% PVC but a further increase in pigment concentration reduces the ability of coating to resist crack propagation. This study was carried out without using any dispersing agent in the paint composition. It may be possible that the addition of dispersing agent can help in increasing the resistance to crack propagation by facilitating dispersion of pigments at higher concentrations.

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