

論文

A Study on the Coating Cracking on a Substrate in Bending II : Experiment

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굽힘모드하에서의 코팅크랙킹의 분석II : 실험

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ABSTRACT

Fracture analysis of coating cracking on a substrate system described in a companion paper was applied and verified by four-point bending tests. The multiple cracking of coating was predicted using a fracture mechanics approach. The strain energy release rate (G) due to the formation of a new crack in a coating was obtained. A crack density vs. strain data of metallic and polymeric substrate was used to get the *in-situ* fracture toughness of coating with respect to various baking time and temperature. The G_c was decreased as the baking temperature and time was increased. This paper gave insight about usefulness of four-point bending test for fracture toughness evaluation of coating and it gave a new method for *in-situ* coating toughness.

초 록

앞 동반논문의 이론에서 기술된 기재위에 입혀진 코팅크랙킹의 파괴역학 분석을 4점 굴곡시험을 이용하여 실증하였다. 파괴역학 접근에 의해서 코팅의 다중크랙킹을 예측하여 코팅층에서 새로운 크랙이 생길 때의 변위에너지 방출량(G)을 구하였다. 여러 건조시간과 건조온도의 변화에 따른 금속 및 고분자 기재위에 입혀진 코팅의 변위에 대한 코팅 크랙밀도의 실험데이터가 *in-situ* 코팅의 파괴인성 값을 구하기 위해 사용되었다. 건조온도가 올라가고 건조시간이 길어짐에 따라 G_c 는 감소하였다. 본 논문은 코팅의 파괴인성 평가에 있어 4점 굴곡시험이 얼마나 유용한지를 보여주며 *in-situ* 코팅인성을 구하는 방법을 제시하였다.

1. INTRODUCTION

In a companion paper [1], fracture analysis was developed for multiple cracking of coating on a substrate system. The expression for the energy

release rate due to the first crack formation in a coating layer is :

$$G = \langle \sigma_{xx,0}^{(1)} \rangle^2 C_3 t_1 \lim_{D \rightarrow 0} Y(D) \quad (1)$$

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where $\langle \sigma_{xx,0}^{(1)} \rangle$ is an average stress in a coating layer, $Y(D)$ is a calibration function of crack density, t_1 is coating thickness and C_3 is a constant which includes material properties of coating and substrate.

In bending loading, the average normal stress in the first layer (coating layer) of a multilayer system is given by

$$\langle \sigma_{xx,0}^{(1)} \rangle = \frac{2\bar{z}_1}{B} E_{xx}^{(1)} \xi_{\max} \quad (2)$$

where \bar{z}_1 is an average distance from neutral axis of sample to the first layer, B is the thickness of the sample, $E_{xx}^{(1)}$ is a modulus of coating layer and ξ_{\max} is maximum strain at the sample surface.

In this paper, we present experimental verification of the new approach to fracture mechanics of coatings given in ref. [1]. The experiments were done on coating/metal and coating/polymer system. These systems showed multiple cracking, coating delamination, or surface embrittlement and we here give a standard methods for predicting *in-situ* coating toughness of multiple cracking from the crack density information on a stress-strain curve.

2. MATERIALS AND METHODS

All coatings used in this study were received from the Du Pont company. The two types of coatings, a solvent evaporation type and a crosslinked type, were used in this study. The mechanical properties of the substrates and the top coats used in this study are given in Table 1.

2.1 Metallic Substrates

Steel substrates of 0.317 cm thickness were supplied by the Du Pont Company already with the primer and top coat of paint. All Du Pont panels with top coat had 1 mil of electrodeposited (ELPO) primer and were pre-baked 30 minutes at

Table 1. Mechanical properties of coatings and substrates. The measured properties were determined using a cross-head speed of 0.05 mm/sec

	Modulus (MPa)	Poisson's Ratio (ν)
Steel	115000	0.28
Polycarbonate	2300	0.37*
ABS	2150	0.39*
PPO-PS Blends (Noryl [®])	2550	0.40*
RKR19004	1660	0.33 [^]
RKR35343	1900	0.33 [^]
RKR35367	2400	0.33 [^]
RC909	1700	0.33 [^]

* Product literature value

[^] Assumed value - not measured

Measure after 24 hours of baking at 130°C

Noryl[®] is a trademark of General Electric

130°C by Du Pont company prior to shipping [2]. The steel substrate and electrodeposited primer were the similar materials that were used in automotive manufacturing. All of the samples were baked for several hours and tested. The primer thickness (1 mil) was thin compared to the clear top coats (6~12 mils). The main function of applying primer is to maximize substrate protection and finish coat adhesion.

2.2 Polymeric Substrates

Three types of polymeric substrates were used. They are polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS) and polyphenylene oxide (PPO) / polystyrene (PS) blends (Noryl[®]).

We chose polycarbonate as our main polymeric substrate because it is one of the toughest polymeric materials, and it is transparent, thus allowing easy experimental observation of coating failures when a transparent coating is applied, and it has some practical applications such as an automotive headlamps lens with protective coating on it. ABS materials are described as tough, hard, and rigid and this combination is unusual for thermoplastics. Protective coatings can be applied to

improve resistance to UV light [3]. The rigid structure of the PPO polymer molecules in PS-PPO blends leads to a material with a high T_g of 208°C. Noryl[®] can be easily applied for automotive in-line painting process.

The polymeric substrates were purchased from a plastic distributor in the form of extruded sheets. No primer was used with the polymeric substrates.

2.3 Coatings

High solids coating (cross-linking type clear coats) and solvent evaporation type coating were used in this study. Coating on a metallic substrate was sprayed using a sprayer. The coating thickness was built-up by spraying multiple coats. Applying coating on a polymeric substrate using a doctor blade with different clearances gave different coating thickness. The substrate thickness and coating thickness were measured using a micrometer.

High solids coatings, RKR19004, RKR35343 and RKR35367, are coatings containing 40% or more solids. Solids are used to reduce volatile organic compound (VOC) emissions, including solvent evaporation. Solvent evaporation type of coating dries solely by evaporation of solvents. A product code of RC909 is the only solvent evaporation type coating used in this study. The polymer is fully formed in the can and, when free of solvent, is relatively hard and not sticky. During the drying process there is no chemical change in the solvent evaporation type of coating.

The following proprietary coatings of Du Pont company were used;

A) RK19004 is a high solids, rigid clear, one-component acrylic/melamine clear coating. More detailed information about the ingredients in this coating and in other coatings can be found [4].

B) RKR35343 is a high solids, rigid clear, one-component acrylic/melamine/silane coating.

C) RKR35367 is a high solids, rigid clear, one-component acrylic/melamine/silane coating.

D) RC909 is a solvent evaporation type coating. It was supplied by the Du Pont company as a 40% by weight solution of polymethyl methacrylate (PMMA) in acetone and toluene. It was applied to polymeric substrates only.

The viscosity average molecular weights of typical poly(methyl methacrylate) Lucite[®] and of RC909 in acetone solvent were determined using a size 100 Canon-Fanske viscometer. The viscosity average molecular weight of RC909 acrylic resin was 75,000 g/mol. This value is approximately one-tenth that of Lucite[®] [5].

2.4 Sample Preparations and Experimental Set-up

The washing and drying procedures of substrates were used to increase the adhesion between coating and substrate. For polymeric substrates, surface modification by grit blast or grinding using #600 sand paper was needed to avoid massive delamination between high solids coatings and the substrate.

Even though less than 1 hour of curing (baking) time is necessary for practical automotive applications with thermosetting type polymers, we used longer baking times to aggravate the coating system and to increase cross-link density.

All the coatings on a metallic substrate supplied by the Du Pont company were sufficiently tough to show no cracking in the "as-received" condition. In order to get clear cracks the coated samples were baked. The baking temperature for the metallic substrates with thermoset coatings was 130°C as recommended by Du Pont and the baking temperatures of coatings for the polymeric substrates had to be lower, depending on the glass transition temperature of the substrate. The baking temperature for PC, ABS, and PPO-PS blends were 110°C, 60°C and 130°C, respectively.

The polymeric substrate samples were baked at different temperature for different amounts of time after painting. In order to study aging, weathering, and cross-link density effects on the coating

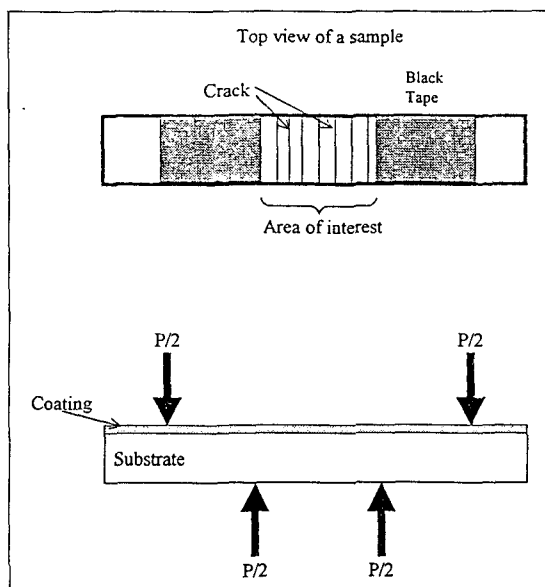


Fig. 1. Four-point bending test geometry

system, we used baking time as a variable. Longer baking times qualitatively simulate more aging, more weathering, or increased cross-link density. After applying solvent evaporation type coating (RC909), polymeric substrates were baked at 60° C as recommended by Du Pont in an oven to evaporate the solvents.

Straight sided polymeric specimens, 100 mm long, 12.5 mm wide, were cut from the coated polymer sheets. The adhesion between RC909 and polymer substrate was very good, even without any surface modification. The support span in the four-point bending geometry was 51 mm and the loading span was one-third of the support span as shown in Fig.1.

All of the static mechanical tests were performed on a Material Testing System (MTS) Model 810 servo-hydraulic testing frame under displacement control mode at ambient temperature and humidity. Stress-strain data were collected using an IBM PC and custom developed software that interfaced the IBM PC to an MTS 464 Digital Display device. All experiments used a cross-head rate of 0.05 mm/s.

2.5 Crack Observation

For coated metallic substrates, usually 10 or fewer cracks were observed. The cracks sometimes caused delaminations and sometimes did not. In polymeric substrates, usually many numbers of cracks were observed than metallic substrates. During these tests, multiple cracking was observed by eye and the strain at each crack appearance was marked by clicking a computer mouse. After the test, the analysis software read the markings to give the strain at the appearance of each crack and strain at initiation of delamination.

Typically 3~10 cracks appeared during the experiment and after those cracks, delaminations appeared in coated polymeric substrates. The initial cracks formed at the end of the linear-region while the later cracks formed in the non-linear region. No additional cracks appeared after the initiation of delamination. Many multiple cracks were observed for thin coatings, but the cracks were so thin that it was difficult to mark a crack initiation. Counting the number of cracks for thin coatings was only possible using an optical microscope after samples bent up to a predetermined strain.

Because the four-point bending tests gave a stable crack propagation pattern, it was possible to accurately record the crack density as a function of increasing strain.

3. RESULTS AND DISCUSSION

Theoretical predictions were compared with the results of the experiments to determine the strain energy release rate (G_c) of the coating. Based on variational mechanics, the *in-situ* fracture toughness of the cracking can be determined using the crack density information [1,5]. A four-point bending test was performed for which the stresses are linear in the thickness direction as discussed in

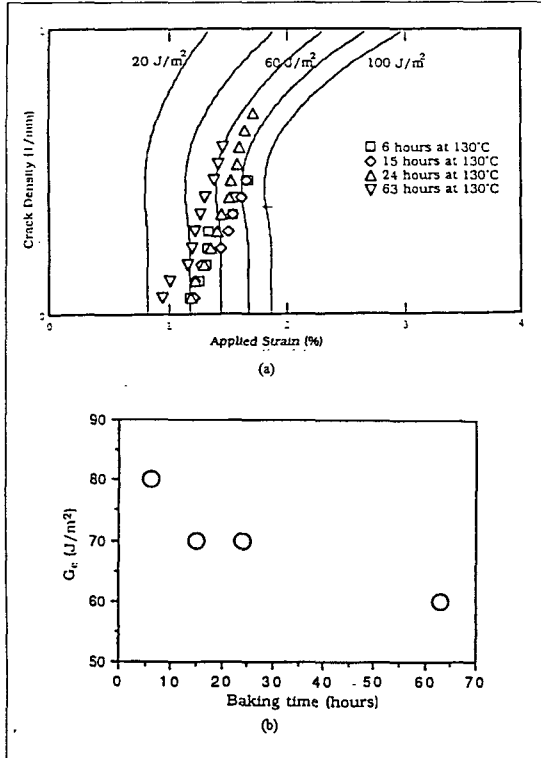


Fig. 2. (a) The crack density vs. applied strain at several baking times for RKR19004. Experimental data are compared with theoretically predicted curves. (b) Critical strain energy release rate (G_c) in RKR19004 coating as a function of baking time

geometry analysis [1].

3.1 Metallic Substrates

The transverse multiple cracks that appeared at small strains in RKR19004 and RKR35343 coatings on steel substrates were ideal for analysis of *in-situ* fracture toughness of the coating. The results of four-point bending tests of steel substrates under various coating conditions and sample histories are given in Figs. 2, 3 and 4.

Plots of crack density vs. strain at several baking times for RKR19004 and †RKR35343 coatings were compared with theoretical predictions as shown in Figs. 2 and 3. The symbols are crack density data for experiments at different baking times and the solid lines are theoretical predic-

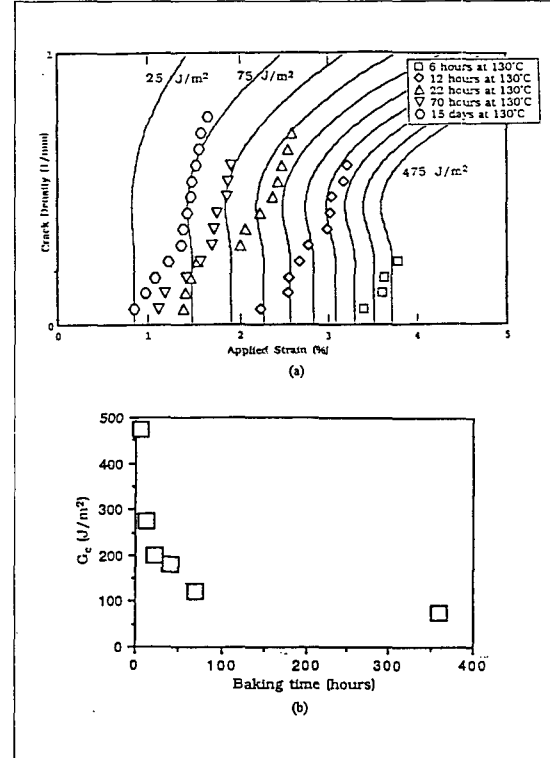


Fig. 3. (a) The crack density as a function of applied strain at several baking times for RKR35343 coating compared with theoretically predicted curves. (b) Critical strain energy release rate (G_c) in RKR35343 coating as a function of baking time.

tions from a bending analysis. The used strain is the maximum strain on the tension side of the beam. The coating modulus of RKR19004 used in these plots, 1660 MPa, was based on a baking time of 24 hours at 130°C. They have become brittle enough to get clear multiple cracks at this baking time.

In RKR19004 coating, as baking time increases, the cracks initiate at lower strain, a trend that is not apparent at the short baking times of 6 and 15 hours. However, the raw crack density data alone shows that the toughness decreases with baking time. The *in-situ* fracture toughness based on first crack initiation was 27 J/m² for 63 hours baking at 130°C. For other shorter baking times the value was near 40 J/m². The theoretical predictions and

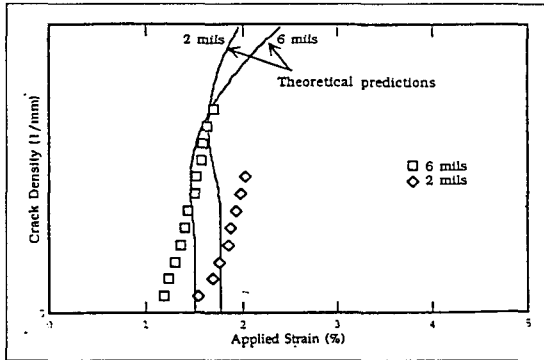


Fig. 4. The crack density vs. applied strain with theoretical predictions using a G_c of 65 J/m^2 . Samples were baked for 24 hours at 130°C

experimental data coincide well for the baking times in this series of tests. Also, good reproducibility of the experimental data with various baking times are indicated by the consistent shape of the data curves; this leads to the conclusion that this test is measuring actual coating properties. A plot of critical strain energy release rate (G_c) of RKR19004 coating as a function of baking time based on Fig. 2(a) is given in Fig. 2(b). The critical strain energy release rate was decreased with baking time.

RKR35343 coating also showed very clear multiple cracking and was a good paint for testing our theory as in RKR19004. Figure 3(a) shows a plot of crack density vs. strain at several baking times for RKR35343 with theoretical predictions. It shows good fits of experimental data with theoretical predictions, especially at higher crack densities. It is claimed that the higher crack density data are better for the characterization of the coating because they are obtained after the flaw-dominated regime. The flaws tended to be used up at relatively low strains, therefore crack density data at higher strains were more reliable. The used RKR35343 coating modulus for stress analysis was based on 24 hours of baking which was 1900 MPa. The critical strain release rate (G_c) vs. baking time for RKR35343 coating is shown in Fig. 3(b). It clearly shows that the *in-situ* fracture

toughness decreased with increasing baking time.

Figure 4 shows fits obtained for RKR19004 coatings that were baked for 24 hours at 130°C using a coating toughness of 65 J/m^2 . The curves are for two coating thicknesses of 2 mils and 6 mils with other parameters fixed. With given G_c , our theory can accurately predict changes in crack density with coating thickness. It shows clearly that thinner coatings start to crack at higher strains but their crack density surpasses that of thicker coatings at high strains. As predicted from our theory, when the coating thickness decreases, more cracks (higher crack density) were observed at high strains. This result is the same as found in refs. [1,6]. The lower crack density in the thicker coating than the thinner coating is due to the higher amount of energy released, the larger crack area, for each crack formation in the thicker coating with a given G_c .

There was a good qualitative fit of the data to the theory in Figs. 2, 3 and 4, but there were also quantitative differences. Theory predicts a rapid crack density increase. The actual experimental results do not increase as rapidly as the theory predicted. One of the reasons may be that the imperfect adhesion between the substrate and the coating. The energy required to create a small localized delaminated area near new cracks was not taken into account in theory. At the final stage of multiple cracking tests, sample starts to delaminate and the delamination eventually results in a smaller number of cracks.

Also, the sudden increase in crack density after the first crack appearance could be related to the isolated coating cracks. When the first crack forms it will release the stresses in the coating near that crack. The stress field away from the crack will return to the far-field stress state and the stress become the same stress which caused the first crack to form. Thus, new cracks will form immediately after the first crack forms. The cracks will be formed continuously until the cracks get close enough that their stress fields begin to inter-

act. This kind of coating failure occurs when the test specimen is homogenous and there is perfect adhesion between the coating and the substrates. The structure heterogeneity and imperfect adhesion make the material property, local coating toughness, vary. The first cracks will form at areas of low toughness, but similar stresses away from these cracks will not immediately cause other cracks. The material imperfection or heterogeneity will cause the crack density to rise slower than predicted by a homogeneous-toughness theory. Instead of abandoning the fracture mechanics analysis for experimental results, we claim that deviations at low strain are measure of the variability of the toughness properties of the coating.

Another possible reason for the deviation between theory and experiments could be the assumption in the theory that all cracks form in the linear elastic region. A typical rigid clear coating on steel substrates showed crack initiation at the end of the elastic region and many of the cracks formed in the plastic region.

3.2 Polymeric Substrates

It is known that mechanical properties of plastics can change dramatically when coated [7-10]. A special example of the automotive application of coated plastics can be seen in the polycarbonate headlamp lenses [11]. The effect of coating application on polymeric substrates was discussed and the *in-situ* fracture toughness of the coatings (G_c) was determined.

The same coatings used on the metallic substrate systems were also used on the polymeric substrates. In addition, a solvent evaporation type coating (RC909) was used. One difference between metallic and polymeric substrate sample preparation was the baking temperature. Polymeric substrates generally required a lower baking temperature.

Figure 5 shows a plot of crack density as a function of applied strain with theoretical curves of RC909/PC system for several different baking

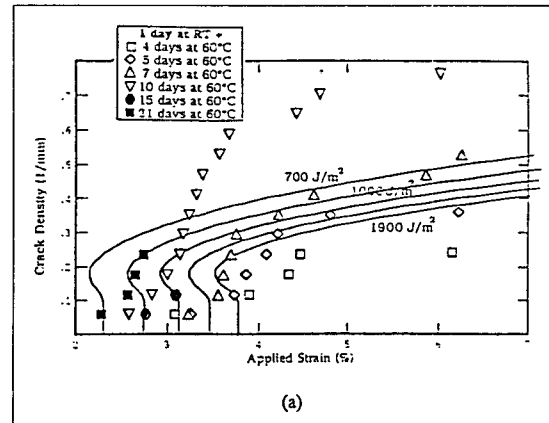


Fig. 5. Crack density vs. applied strain for RC909 (6 mils) / PC (228 mils) system with theoretically predicted curves

times at 60°C. The solvent evaporation coating and polycarbonate substrate system was our model system for applying fracture mechanics to a coating/substrate system. For the sample with 4 days of drying at 60°C, the rate of crack number increase was lower than the theoretical curves. This deviation might be due to microcracking between big cracks that occurred in the samples dried only for four days. The effects of microcracking on crack density are discussed in elsewhere [12]. The sample with 10 days of baking gave very clear multiple cracking occurred and the crack density was higher than the theoretical curves.

Because the fits between theoretical curves and experimental results were not as good as for metallic substrates, it was difficult to pick the best fit for polymeric substrates. The theoretical predictions on crack density with strain for polymeric substrate showed a region where the crack density increasing as the strain decreasing. In real experiments, the crack density always increase as the strain increase. Therefore, when analyzing the experimental results, the region should be ignored. The initial vertical rise of the theoretical predictions can be extended up until it intersects the curve again at which the crack density

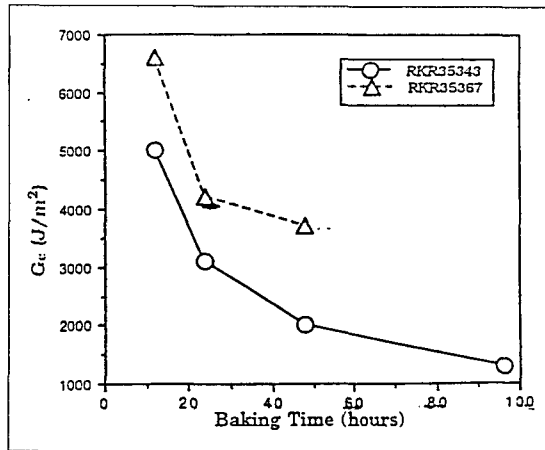


Fig. 6. Critical strain energy release rate (G_c) vs. baking time for RKR35343 and RKR35367 coatings on a PC substrate. Sample was baked at 110°C

increase with the strain increase.

The G_c of RC909 coatings was in a range of 700 J/m^2 to 1900 J/m^2 and the samples were failed in the linear-elastic region. The G_c values were higher than that of the tension experiment, 250 J/m^2 , for similar drying conditions [12]. The higher strain energy release rate (G_c) of RC909 coating, however, is still a reasonable value for PMMA toughness [13].

The samples with 15 days of baking and 21 days of baking exhibited surface embrittlement (filled symbols in Fig. 5(a)). The embrittlement phenomenon is one of the drawbacks of applying coatings to polymeric substrates [7,8,10]. Embrittlement occurred when one of the cracks in the coating penetrated the substrate, leading to sample failure. The embrittled samples failed in a brittle and rapid manner corresponding to a sharp decrease in load. The surface embrittlement was observed with other polymeric substrates.

The G_c of RC909 coating was decreased as baking time increased. Baking at high temperatures, accelerated weathering, or long aging times at room temperature can be thought of as an energy absorbing process. When an organic polymer is subjected to heat or radiation, the absorbed energy induces chemical changes in the polymer that

affect its physical and chemical properties. Irradiation of PMMA causes main chain scission to occur, resulting in a decrease in molecular weight of the polymer in exposed areas [14]. It is speculated that the molecular weight of RC909 decreased as baking time increased. This is consistent with the decrease of G_c with baking time since a lower molecular weight polymer has the lower fracture toughness.

The G_c values by a bending analysis as a function of baking time for RKR35343 and RKR35367 coatings are given in Fig. 6. The G_c 's found were higher than with the same coating on metallic substrates. A possible reason for the higher G_c values may have been the lower baking temperature (110°C) than the suggested baking temperature for RKR35343 and RKR35367 coatings (130°C). A lower baking temperature probably produced a lower cross-link density, led to a less brittle coating and a higher G_c value. Other possible factors include cracking after yielding and different residual stress build-up on metallic and polymeric substrates. The G_c value was decreased as baking time increased. The G_c 's of RKR35367 were higher than those of RKR35343 at the same baking time. This relation was the same as the one found for metallic substrates.

ABS showed yielding and stress whitening by bending tests after baking at 110°C without any coating and there was no surface embrittlement. However, coated ABS samples showed surface embrittlement. The solvent evaporation type coating (RC909) was applied to the ABS substrate using a doctor-blade. The sample panel was air-dried 2 days and then baked 2 weeks at 50°C . The RC909 coating showed clear multiple cracking and a few cracks in the elastic region by four-point bending test. This is one of the few samples that showed all cracks in the linear elastic region.

Figure 7 shows the crack density as a function of applied strain for an RC909/ABS sample along with theoretical curves. The G_c value based on our theory was 550 J/m^2 . The fit was among the best

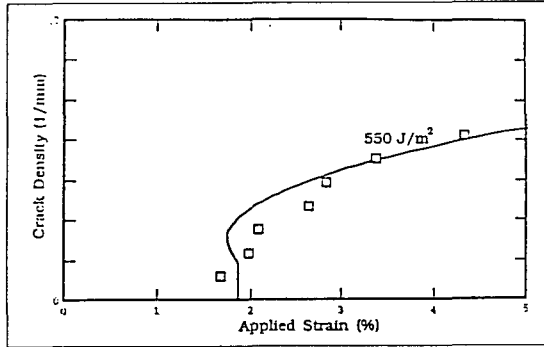


Fig. 7. Crack density as a function of applied strain for the RC909 (7.8 mils)/ABS (255.8 mils) system with theory predicted curve for $G_c=550 \text{ J/m}^2$. The sample was dried 2 days at room temperature and baked 2 weeks at 50°C

obtained. This G_c value is about two times higher than the value obtained with tension tests using the same coating system but for different substrates [4,5]. It is still comparable with previous results for PMMA [13]. This sample had no microcracks. Good fits of experimental data to theoretical curves for samples without microcracks were also observed elsewhere [5].

Careful observation of the load-displacement curve shows a slight drop in load corresponding to the appearance of each crack. The cracks in the RC909 coating were arrested, but they showed some penetration into the ABS substrate. Finally, one of the arrested stationary cracks propagated further into the ABS substrate and the sample failed catastrophically as in polycarbonate substrate. Maybe, the solvent sensitivity of ABS led to the surface embrittlement. Another factor could be stress concentration effects of cracks in the coating layer [9]. Once a crack is generated, stress concentration occurs at the crack tip. Once the critical stress is exceeded one of the stationary cracks can propagate into the polymeric substrate. Even though a relatively low baking temperature (50°C) was used, the sample showed surface embrittlement.

In order to see the substrate effects, RC909 coating on the ABS and Noryl^{GE} substrates were

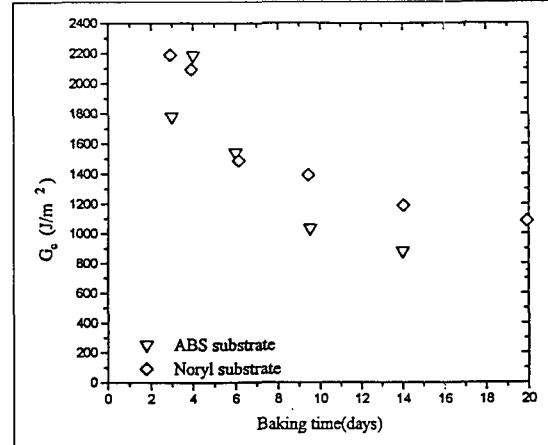


Fig. 8. Critical strain energy release rate (G_c) vs. baking time for RC909 coating on (a) an ABS substrate, (b) Noryl^A substrate.

tested. Figure 8 shows strain energy release rate (G_c) vs. baking time of RC909 coating on an ABS and Noryl^A substrates. The critical strain energy release rates of the same coating at the same baking time were almost same for two different substrates. It implies that the substrate effects of RC909 coating between ABS and Noryl^A substrate is small.

4. CONCLUSIONS

Multiple cracking of coatings on metallic or polymeric substrates was compared with the theoretical predictions to determine *in-situ* coating toughness. With baking, cracking often occurred, allowing us to analyze coating toughness as a function of baking time. The four-point bending tests allowed stable crack propagation, formation of clear transverse cracks, and an accurate crack density measurement with increasing strain.

The strain to high-crack density data was used to measure the strain energy release rate of coatings on metallic and polymeric substrates. When crack density vs. applied strain information of the energy release rate theory was compared to the

experimental results for a solvent evaporation type coating on polymeric substrate sample with few microcracks, the best agreement was obtained among the samples used in this study. However, for rigid RKR coatings on steel substrates, the theory predicts a density increase that is more rapid than is experimentally observed.

The cracking behavior of baked coatings was used to predict the durability or long time cracking behavior of these coatings. A decrease in coating toughness with increasing baking time was found. Using long baking times is physically reasonable as a qualitative simulation of coating aging or weathering.

The energy release rate theory did a reasonable job of fitting the best data (i.e. multiple cracking data). It is useful for translating experimental results into a physically meaningful property n coating fracture toughness G_c .

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