

Effect of the Pigment–Polymer Interfacial Interactions on the Mechanical Performance of Automotive Topcoat Layers

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ABSTRACT: The study of the effect of interfacial interactions on the mechanical performance of a selected automotive topcoat system has been undertaken. The investigation concerned interactions that arise in acrylic-melamine/pigment assemblies. The pigments were designed to have different surface treatments. Three types of TiO₂ pigment, one type of C. I. Pigment Green 7, and a chrome oxide pigment were used in this research. Information regarding the surface characteristics of the pigments and also of the polymer was obtained by Inverse Gas Chromatography (IGC) technique. The pigments, at different particle volume concentrations, were dispersed into the polymeric matrix with the aid of their related additives. The cured coating samples were

subjected to tensile stresses. The maximum stress that each sample withstood before breakage was recorded. Two different types of behavior were observed for coating composites that contained one of the pigment forms, at different particle volume concentrations. Finally, the data obtained from the IGC studies were used to support the results obtained from tensile testing. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2261–2268, 2006

Key words: interfacial interactions; inverse gas chromatography; particulate-filled composites; automotive topcoat system; tensile mechanical testing

INTRODUCTION

Organic coatings are used in the automotives industry, mainly for two purposes: to protect the substrate and to improve the appearance. These objectives are achieved by applying a multilayer system onto the substrate. Each layer, each with its specific responsibilities, has a different chemistry provided by the formulation. Incorporation of a pigment in each layer fulfils a different purpose. Thus, in a topcoat the pigment is used mainly for decorating and UV protection, while in primer it is added mainly for corrosion protection. To perform these functions effectively, the coating multilayer must possess certain mechanical properties. It is essential to know the dependence of such properties on the composition if an understanding of performance–composition relationship is to be obtained. Pigments, like all inclusions, are known to induce stress concentrations in heterogeneous polymer systems. As a consequence, the mechanical performance of polymer can be affected, either positively or negatively, by pigment and/or filler introduction.^{1–4}

To evaluate this effect, the ultimate tensile properties are of primary importance, giving information on

the maximum allowable load to composite failure and to the final break.^{5–7}

Different models have been developed for predicting the mechanical performance of particulate-filled composites.^{8–13} For some systems, the ultimate tensile strength decreases monotonically as the particle volume concentration (pvc) increases. For other systems, on increasing the pvc, the ultimate tensile strength increases, reaching a maximum before falling off. For the former behavior type, the assumption is that the discrete particles are detached from the matrix.

Practically, the volume occupied by the particle acts as a void, resulting in a decrease in the load bearing cross-sectional area of the composite. For the latter type, because of good interaction between the included species and the matrix, a portion of the stress is transferred onto the particle to become dissipated. On combining these two effects, it appears that the level of interaction and adhesion between the included species and the matrix is a controlling factor in the composite performance under mechanical stress.

For a better understanding of the role of interfacial interactions, between the particle and the matrix, a simplified model based on a parallel series of springs is presented here. In Figure 1(a) a unit cell of polymeric matrix is represented by a spring with specific constant k_m . The constant of proportionality k appears in Hook's law for springs

$$F = k_m x \quad (1)$$

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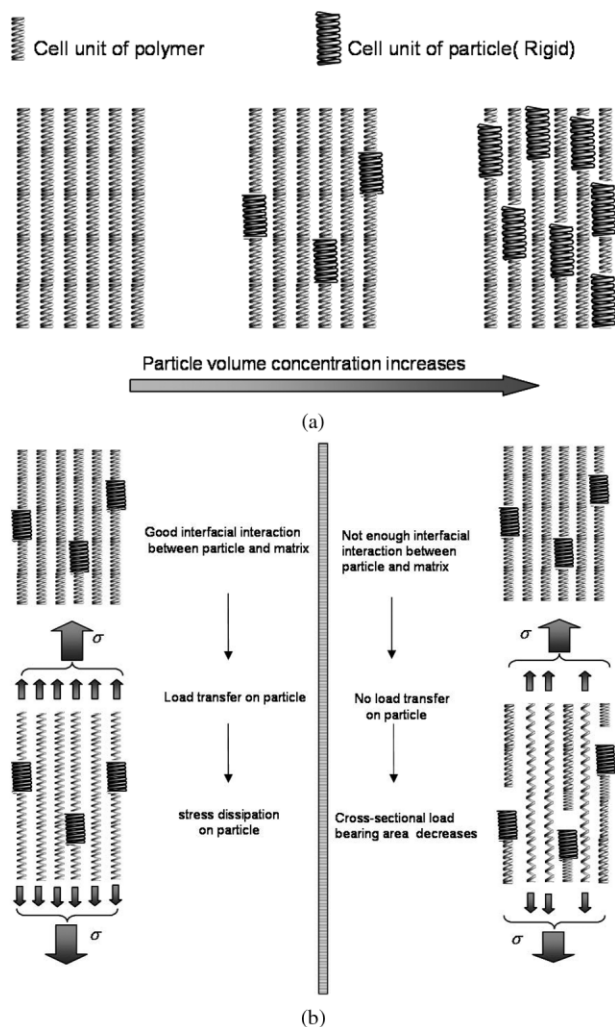


Figure 1 (a) Polymer composite shown as parallel series of springs at different particle volume concentrations. (b) The effect of interfacial interaction between particle and matrix on the performance of composite under mechanical stress.

Here, F is the applied force and x is the displacement from equilibrium. The whole matrix system is shown as parallel series of spring units attached to each other. In reality, one deals with a complicated three-dimensional crosslinked system instead of the simple model given here.

The rigid particle is also shown as a spring but with a bigger constant k_p representing the pigment. As the particles get into the matrix, a volume portion of matrix is replaced by the particles [Fig. 1(b)].

Two composite systems are depicted in Figure 1. For one of them [Fig. 1(b)], there is an implied degree of good interaction and adhesion between the particle and the matrix. For the other, there is an insufficient level of interaction between the particle and the matrix. When the whole composite system undergoes a tensile stress, as well as yielding, a different scenario is played out for each system. For the system with good interactions, a part of load stress is transferred onto

the rigid particle via the interface. The rigid particle is stronger than the same volume of polymer under stress. Therefore, for this system, the ultimate tensile strength is expected to improve relative to that of the unfilled polymer system. For the system in which there is no interaction between the particle and the matrix, the particle acts as a void, resulting in a detrimental effect to the ultimate tensile strength of the filled composite in comparison to the that of unfilled polymer. In this research, the effect of the introduction of one of three types of rutile TiO_2 pigment (each of which had different surface treatment), of C. I. Pigment Green 7, and of pigment chrome oxide into a topcoat polymer coating system is investigated in an evaluation of the interfacial interaction contribution to the mechanical properties of filled system. Because of different surface characteristics, the strength of interaction between each pigment particle and the polymer would be expected to be a function of the surface treatment of the pigment. To quantify this strength of interaction, the inverse gas chromatography (IGC) technique was employed.

The growing awareness of the importance of solid surfaces, interfaces, and interphases has led to the development of IGC as a useful technique in evaluating the potential for interaction of different components of polymeric blends, composites, and multicomponent polymeric systems. The relationship between intermolecular interactions and system properties is particularly important in polymer compositions, bearing in mind the variety of polymers, pigments, and additives that are used to achieve desired performance requirements. Intermolecular forces that are operating between molecular segments of polymers and at particulate interfaces are frequently cited in the literature^{14–17} as being responsible for the properties of the system as a whole. Control of Lewis acid/base interactions has gained increasing significance in industrial practice^{18,19} for optimizing the performance of polymer composites.

The main difference between conventional gas chromatography (GC) and IGC lies in the fact that in IGC the species of primary interest are not the volatile components injected but are rather the material acting as the stationary phase, typically a powder, fiber, or film. This material may be packed directly into the column. It may be coated onto a suitable support or coated onto the walls of the column. This allows the investigation of the interactive nature via the degree of interaction with well-characterized volatile liquids/vapors ("probes"). Quantification of this interaction may be achieved by the determination of the retention time, t_r , for a given probe.

The method of calculation of the Lewis acid/base interaction parameters, k_a and k_b , as well as the dispersive component of surface free energy, γ_s^d , from the retention time, t_r , can be found in the literature.^{20–23}

In this study, the effects of the surface characteristics of different pigments and the establishment of whether or not the pigment could play a significant role in the mechanical performance of cured pigmented coating layers have been investigated.

EXPERIMENTAL

Three types of TiO₂ pigments were obtained from Huntsman Tioxide (Billingham, UK), with different surface treatments. These were TiO₂/5.5, TiO₂/7.2, and TiO₂/9. The pigments were similar to conventional TiO₂. The exception was that there was a different content of sulfonic acid groups present on the surface of the particles. The particles varied in the decreasing order of TiO₂/5.5, TiO₂/7.2, and TiO₂/9. As may be appreciated from Table I, the numbers 5.5, 7.2, and 9 relate to the pH of the aqueous medium from which the particles were separated after prior dispersion.

Pigment green chrome oxide/M100 was provided by Elementis Chromium (Eaglescliffe, Stockton on Tees, UK), and BASF (BASF AG, Ludwigshafen, Germany) provided C. I. Pigment Green 7.

A thermoset acrylic polymer solution of Setalux 6100 was provided by Akzo Nobel (Akzo Nobel Resins bv, AB Bergen op Zoom, The Netherlands). This was used as the matrix, in combination with a melamine-based polymer, Setamine MS-152, which was also provided by AkzoNobel, used as a crosslinker. The mixture ratio of acrylic to melamine component was 3/1 by weight. The curing was carried out at 150°C for 30 min.

Inverse gas chromatography

To acquire information concerning the characteristics of the surfaces of the pigments and also the polymer, the IGC technique was utilized. A Varian gas chromatograph (Model 3300) was used with an external carrier gas flowmeter.

A U shape stainless steel tube of 50 cm length and 4 mm inner diameter was used to contain the material of interest as the stationary phase and support material, Chromosorb P. The column preparation is important. Details of effective column preparation can be found

TABLE I
The specifications of the three TiO₂ pigments and their surface treatment materials

Pigment	pH	%SO ₃	%Al ₂ O ₃	%ZrO ₂	Given name
M574/302/A	5.5	>0.27	2.46	0.37	TiO ₂ /5.5
M574/302/D	7.2	0.02	2.45	0.35	TiO ₂ /7.2
M574/302/G	9	0.03	2.43	0.37	TiO ₂ /9

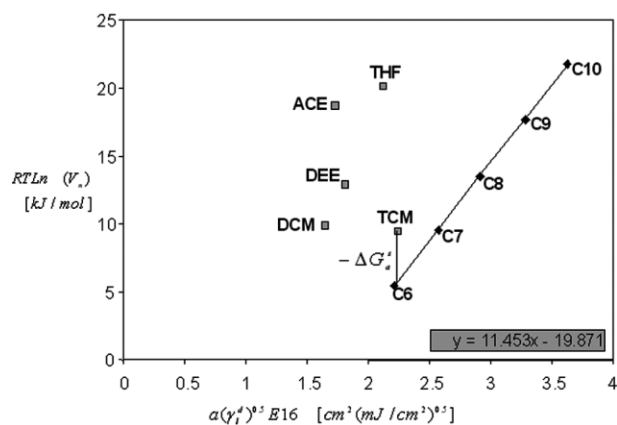


Figure 2 Surface free energy of adsorption $RT \ln(V_n)$ versus $a(\gamma_s^d)^{0.5}$ of *n*-alkanes and polar probes on the surface of TiO₂/9, at 373K.

in the literature.²⁴ The pigment and the Chromosorb at the ratio of 2/1 were mixed and packed uniformly into the column. Prior to IGC evaluation, the polymers first were coated on Chromosorb P at a 15% loading (by weight) in a rotary evaporator from a diluted polymer solution in acetone. Then, the polymer-coated catalysts were packed into the column. Using helium as the carrier gas, at the fixed flow rate of 15 cm³/min, pulses of 2 μL of well characterized molecular probes were injected into the column. The time taken for the pulse to elute the column was measured by FID detection. The IGC experiments were made at infinite dilution, approaching conditions where Henry's law is obeyed.

The nonpolar probes were *n*-hexane (C-6), *n*-heptane (C-7), *n*-octane (C-8), *n*-nonane (C-9), and *n*-decane (C-10), and the polar probes were dichloromethane (DCM), trichloromethane (TCM), diethyl ether (DEE), acetone (ACE), and tetrahydrofuran (THF). To give good precision in the measured retention times, every injection was triplicated. This procedure was repeated at different temperatures ranging from 70 to 120°C in increments of 10°C. Processing of the data^{20–23} led to the acquisition of the total free energy change at the related temperature. Figure 2 shows the free energy change versus $a(\gamma_s^d)^{1/2}$ for the TiO₂/9 pigment at 100°C. Here, a and γ_s^d are the molecular surface area and the dispersive surface free energy of the gas probes, respectively. The data show that the values obtained from adsorption of nonpolar probes on the stationary phase, lie on a linear line from which the dispersive component of surface free energy of pigment surface can be calculated, via the slope. The distance between points representing the polar probes and the linear nonpolar line at a $a(\gamma_s^d)^{1/2}$ value shows the specific component of free energy change for the probes adsorbed onto pigment surface. Having the specific component of the free energy of adsorption,

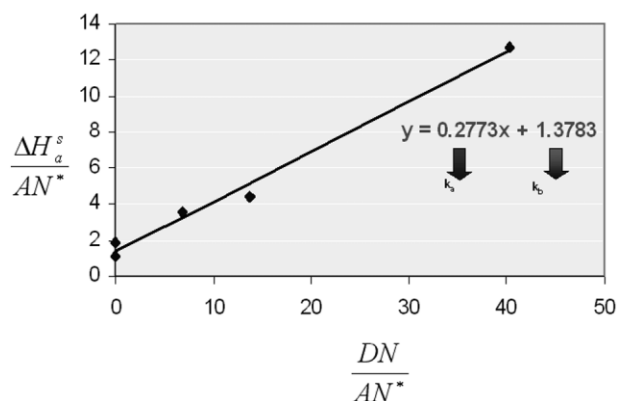


Figure 3 Determination of k_a and k_b as acidic and basic components of the pigment $\text{TiO}_2/7.2$ (from eq. 2^{20–23}).

allows one to find the specific components of enthalpy of adsorption, ΔH_a^s , and entropy of adsorption, ΔS_a^s , through eq. 2.

$$\Delta G_a = \Delta H_a - T\Delta S_a \quad (2)$$

Here, T is the absolute temperature. The relationship, $\frac{\Delta G_a^s}{T}$ versus $\frac{1}{T}$ allows the slope and intercept to be ΔH_a^s and ΔS_a^s , respectively.

The last step in calculating k_a and k_b , as described in the Introduction, is to plot $\frac{\Delta H_a^s}{AN^*}$ versus $\frac{DN}{AN^*}$ from which k_a and k_b can be obtained as the slope and the intercept, respectively.^{20–23} Here, DN and AN^* are Gutmann's donor and modified acceptor numbers, respectively. Figure 3 shows how these quantifications were developed for the pigment $\text{TiO}_2/7.2$. For every sample, the procedure mentioned earlier was followed to extract k_a and k_b as the Lewis acidic and basic characteristics of materials under study.

Coating formulation and mechanical properties

Pigment particles at different particle volume concentrations of 0–50%, in increments of 10%, were introduced into the acrylic polymer solution after the addition of the Disperbyk 110 additive (2% of pigment by weight) for the systems containing pigments $\text{TiO}_2/5.5$, $\text{TiO}_2/7.2$, and $\text{TiO}_2/9$, Disperbyk 161 (40% of pigment by weight) for the system containing C. I. Pigment Green 7, and Disperbyk 180 (10% of pigment by weight) for the system containing chrome oxide/M100. The mixing lasted for 90 min. The mixing was followed by ballmilling for 24 h. At this stage, the melamine resin crosslinker was mixed into the matrix. Then films of the compositions were applied on a support substrate consisting of Whatman filter paper (No. 1) that had been precoated with a 50 μm layer of the parent acrylic melamine polymer, and then cured

at 150°C for 30 min. This was to minimize the penetration of the pigmented fluid dispersion into the pores of the filter paper.

After the application of the pigmented coating dispersion at a thickness of 100 μm , curing at 150°C for 30 min was carried out. For each pigment type and loading level, 6 samples (size, 75 × 25 mm²) were prepared for tensile testing. The samples were mounted into a Satec T-1000 tensile tester and pulled apart at a 0.1 mm/min crosshead speed until the sample yielded and then broke.

RESULTS AND DISCUSSION

The dispersive and the specific components of the TiO_2 pigments used and also of the acrylic polymer and the melamine crosslinking polymer, obtained by the IGC technique, are given in Table II. A comparison between the k_a and k_b values for the three pigments (Table II) shows that the samples have different Lewis basic characteristics, while such a significant difference is not seen in the Lewis acidic characteristics.

For example, the $\text{TiO}_2/9$ pigment has a k_b value of 1.50. The value for the $\text{TiO}_2/5.5$ pigment is 0.27. The cause of such a difference in the specific characteristics of the two pigment surfaces can be the type and amount of material that is present on the surfaces introduced by the surface treatment stage (Table I). The $\text{TiO}_2/9$ pigment was pretreated with inorganic materials such as Al_2O_3 and ZrO_2 . Therefore, the pigment surface represents the Lewis characteristics that are dominantly basic. For the $\text{TiO}_2/5.5$ pigment, the surface characteristic shifts from those of $\text{TiO}_2/9$ and $\text{TiO}_2/7.2$ because of the presence of more SO_3 groups on the pigment surface (Table I). As a result, there is a change in the specific characteristics of k_a and k_b (Table II). Putting together the γ_s^d values of three TiO_2 pigments with their k_b values, (Table II) illustrates a trend in which, as k_b increases, γ_s^d increases too. However, such a trend does not seem to be followed for k_a .

TABLE II
The Dispersive Components of Surface Free Energy and k_a and k_b Values for the Different Pigments and for the Acrylic Polymer and Melamine Crosslinker, and the Pigment–Polymer Pair Interaction Parameter I_{sp} Introduced by Schreiber et al.²⁵

Sample	γ_s^d at 373 K (mN/m)	k_a	k_b	I_{sp}
$\text{TiO}_2/5.5$	43.819	0.20	0.27	0.51
$\text{TiO}_2/7.2$	85.010	0.27	1.37	0.73
$\text{TiO}_2/9$	90.486	0.25	1.5	0.73
C. I. Pigment Green 7	95.98	0.13	0.38	0.46
Chrome oxide/M100	24.05	0.031	0.32	0.29
Acrylic polymer	22.562	0.05	0.62	
Melamine crosslinker	21.672	0.09	1.05	

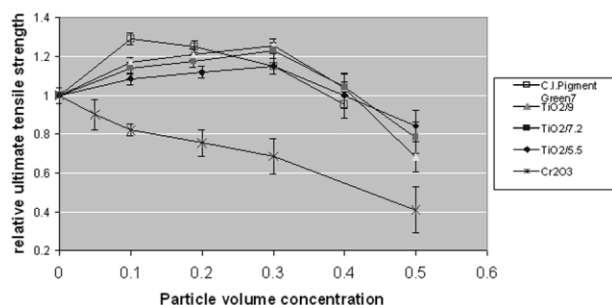


Figure 4 The relative ultimate tensile strength of Whatman No. 1 paper coated with a polymer composite filled with three types of TiO₂ at different particle volume concentrations (The values relative to that of the un-pigmented coating equivalent).

The information concerning the surface characteristics of C. I. Pigment Green 7 and also pigment chrome oxide/M100 is seen in Table II. C. I. Pigment Green 7 shows a big dispersive component of the surface free energy, while pigment chrome oxide/M100 unexpectedly has a very small value for the dispersive component of surface free energy. This was rationalized by the information from the manufacturer regarding the pigment surface treatment, using a solution of cellulose derivative to remove Cr⁶⁺ from the pigment surface. The presence of cellulose derivative on the pigment surface can be the reason for the low dispersive component of the surface free energy.

Neither C. I. Pigment Green 7 nor pigment chrome oxide/M100 have strong specific characteristics as seen in either the Lewis basic k_b constant or the Lewis acidic constant k_a .

Summarized data of interest regarding the acrylic system and the melamine system polymers are also given in Table II. The dispersive component for these series of materials under investigation is smaller than that of the pigments discussed earlier. This is because of the organic nature of the macromolecular surface treatments. For the specific components, in each polymer sample, k_a is smaller than k_b , showing that the polymers are bifunctional. However, for both, the basic character is stronger than the acidic character.

Tensile characteristics of pigmented coatings

Figure 4 shows the relative ultimate tensile strength of cured filled coatings that were applied on Whatman No. 1 paper to that of unfilled equivalent, at different particle volume concentrations. Two types of behavior are seen in Figure 4; for the first type representing the group of coatings that contain pigments TiO₂/5.5, TiO₂/7.2, TiO₂/9, and C. I. Pigment Green 7 individually, the relative ultimate tensile strength of the coatings increases as the particle volume concentration increases, reaching a maximum before falling at

higher loadings. For the other type of behavior representing the coating containing the pigment chrome oxide/M100, the relative ultimate tensile strength starts to decrease gradually on increasing the pvc. Introduction of the TiO₂ pigments with their different surface characteristics resulted in a difference in the mechanical tensile performance. Such observations have their origins in the difference in the interfacial interactions between the included species and the matrix, caused by the pigment surface treatment. Introduction of TiO₂/9 and TiO₂/7.2 pigments gave better results when statistically compared with those given by TiO₂/5.5 pigment up to a particle volume concentration of 30%.

Figure 4 also shows that the TiO₂/9 pigment performed slightly better than did TiO₂/7.2 over this range of particle volume concentrations (pvc). However, since their error bars overlap, the superiority of TiO₂/9 pigment to TiO₂/7.2 in strengthening the polymeric matrix below the pvc of 30% cannot be claimed statistically. Moving from a pvc of 30% to that of 50% (Fig. 4) does not show any significant difference between the coatings that contain each of the three types of TiO₂ pigments. Three points are noteworthy:

1. For all three pigments, the relative ultimate tensile strength falls significantly beyond a critical pvc.
2. The coating that contains the TiO₂/5.5 pigment experiences a more gradual decrease in comparison with the steep declining behavior of the coatings containing TiO₂/9 and TiO₂/7.2 pigments.
3. Considering the whole range of pvc, the error bars in the declining part of curves are much greater than those in the increasing part at lower particle volume concentrations (i.e. <30%).

For the system containing C. I. Pigment Green 7, the relative ultimate tensile strength increases up to particle volume concentration of 10%; at this point the composite system achieved the best performance among all systems evaluated in this study, exceeding even the maximum peak values of the systems containing the TiO₂ pigments. Also, for the system containing C. I. Pigment Green 7, the maximum peak is achieved at a lower pvc when compared with the systems containing the TiO₂ pigments. Beyond the pvc of 10%, for the coating containing pigment Green 7, the tensile mechanical performance of the system decreases as the particle volume concentration increases (Fig. 4).

For the systems containing the pigment chrome oxide/M100 the second type of behavior is represented in the ultimate tensile strength. The tensile strength starts to deteriorate as the particle volume concentration increases. The difference in the relative ultimate tensile strength of the substrate that had been coated with the medium filled with the different pigments at different particle volume concentrations was considered. The difference can be explained by considering

the difference in the dispersive surface free energy of three pigments mentioned in Table II. $\text{TiO}_2/5.5$ has much less dispersive surface free energy than those of $\text{TiO}_2/9$ and $\text{TiO}_2/7.2$. Between these two, the dispersive surface free energy of $\text{TiO}_2/9$ pigment is slightly greater than that of $\text{TiO}_2/7.2$. Among the pigments used in this study, C. I. Pigment Green 7 and pigment chrome oxide/M100 had the greatest and the least dispersive component of surface free energy, respectively. The work of adhesion between the two species, considering just the dispersive components, can be calculated from the Fowkes' equation²⁶

$$W_A = 2\sqrt{\gamma_s^d \gamma_i^d} \quad (3)$$

Here, γ_i^d is the dispersive surface free energy of the polymer, and γ_s^d is that of pigment. The greater the dispersive surface free energy of pigment, the greater is the work of adhesion between the two species. Therefore, the strength of interaction between polymer and these pigments would be expected to be in the descending order of C. I. Pigment Green 7, $\text{TiO}_2/9$, $\text{TiO}_2/7.2$, $\text{TiO}_2/5.5$, and chrome oxide/M100.

On the other hand, various workers have shown that a stress concentration is developed around inclusions as they get into the matrix [^{27,28}]. Under external forces, the zones with higher stress concentration would be at the risk of yielding or disbanding. On the basis of this concept, it could be claimed that the greater the degree of interaction or adhesion between inclusion and matrix, the more resistant the composite system would be to the external tensile stress application.

The reasoning used to explain the behavior of the first group (i.e., the systems containing C. I. Pigment Green 7, $\text{TiO}_2/9$, $\text{TiO}_2/7.2$, and $\text{TiO}_2/5.5$ individually) can be applied to particle volume concentrations up to their maximum peak of relative ultimate tensile strength. Beyond this, there is a different explanation for the origin of the mechanical performance data presented in Figure 4, irrespective of what the pigment type is.

This concentration is considerably less than the so called critical pigment volume concentration, at which the mechanical tensile strength of coating starts to fall from its peak as the particle volume concentration passes this point.^{29,30} The following are possibilities for this premature decrease:

1. The formation of aggregates and flocculates as the pvc increases. The particles come much closer to each other, which results in an increase in possibility of aggregate formation.

2. The introduction of air and voids into the system. At a higher pvc, there is more chance of air entrapment in the finally cured coating because of problems associated with poor wetting, mixing, and agglomer-

ate introduction. Not only can these voids assist the mechanical failure, acting as weak points, they can also initiate rupture.

3. Discontinuity in the matrix

For the systems containing the pigment chrome oxide/M100 (i.e., the second group) the work of adhesion between the particle and the matrix would be the weakest from the strength point of view, as implied by the smallest value in Table II obtained for chrome oxide/M100.

There is also another possible explanation of the inferior behavior of the system containing chrome oxide/M100. This behavior could be due to the poor wetting of the pigment surface by the polymer during the incorporation of pigment into the polymeric system. The pigment has the γ_s^d of 24.05 mN/m, which is only slightly higher than the γ_i^d value of the polymer (~22 mN/m). To have complete wetting, the adsorbent pigment needs to have a marginally higher value for the dispersive component of surface free energy than that of the adsorbate polymer. For complete wetting, this requirement must be met.

The interaction parameter introduced by Schreiber and coworkers²⁵ was calculated for the pigment-polymer pairs (Table II). The k_a and k_b values for the acrylic polymer/melamine crosslinker mixture were interpolated from the k_a and k_b values of the acrylic polymer and the melamine crosslinker with the mixture ratio of 3/1. It shows that there is a correlation, to some extent, between the interaction parameters introduced by Schreiber et al. and the tensile properties. However, the interaction parameter for the combination of C. I. Pigment Green 7 with the acrylic-melamine polymer matrix does not represent the ultimate tensile strength behavior of the system. This might be due to the exclusion of the dispersive component of surface free energy in calculating the interaction parameter. The dispersive component of surface free energy for C. I. Pigment Green 7 has the highest value in Table II.

There are researchers who do not support the concept that such interaction parameters represent the real interaction appropriately.³¹ Santos et al. have suggested that the data obtained by the IGC technique, such as k_a and k_b , would be more appropriate to interpreting interaction phenomena and also the final properties of the system.

Figure 5 shows the SEM image of a coating that contains the $\text{TiO}_2/5.5$ pigment at the particle volume concentration of 50%. The SEM shows how the pigment particles are packed close to each other in the system. From the image, some patterns of aggregation and some voids are visible. For the other two coating systems containing $\text{TiO}_2/9$ and $\text{TiO}_2/7.2$ the SEM images look relatively similar to that of the system containing $\text{TiO}_2/5.5$.

Figure 6 shows the SEM image of the coating that contains pigment chrome oxide/M100 at 50% by volume after curing. Some aggregates and agglomerates are clearly visible in this image. Comparison of the Figure 6 with Figure 5 shows that the degree of dispersion for the system containing chrome oxide/M100 is inferior to degree of dispersion containing $\text{TiO}_2/5.5$, which represents the first group.

The difference in the degree of dispersion between the systems containing C. I. Pigment Green 7, $\text{TiO}_2/9$, $\text{TiO}_2/7.2$, and $\text{TiO}_2/5.5$ individually, and the group containing pigment chrome oxide/M100 could be another reason for the better ultimate tensile performance of the former group of the coatings relative to that of the latter group of coatings.

CONCLUSIONS

Different types of pigment were introduced into an acrylic-melamine polymeric system that is used for automotive topcoat. Two types of behavior have been identified, which have been a basis of the relative ultimate tensile strength of filled coating systems at different particle volume concentrations. For systems containing C. I. Pigment Green 7, $\text{TiO}_2/9$, $\text{TiO}_2/7.2$, and $\text{TiO}_2/5.5$ individually, the relative ultimate tensile strength of the filled coating increased to a maximum at a certain particle volume concentration before falling. Coatings containing the $\text{TiO}_2/9$ and the $\text{TiO}_2/7.2$ gave superior performance when compared with that containing the $\text{TiO}_2/5.5$ at particle volume concentration up to 30%. The system containing C. I. Pigment Green 7 showed the best ultimate tensile strength among all the filled systems in this study. However, the maximum tensile strength occurred for a lower pvc of 10% when compared with that of systems containing TiO_2 pigments. This effect was rationalized

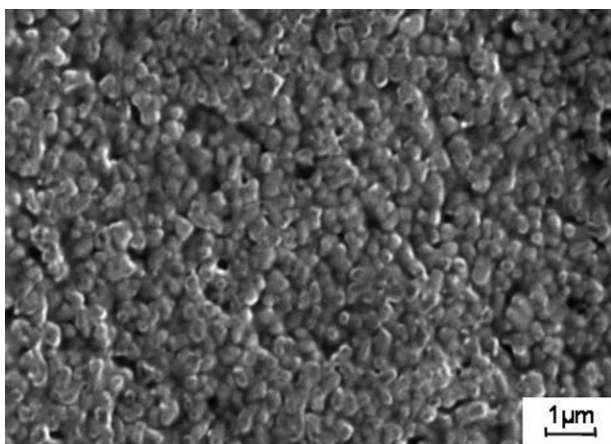


Figure 5 The SEM image of coating containing $\text{TiO}_2/5.5$ pigment at a pvc of 50%.

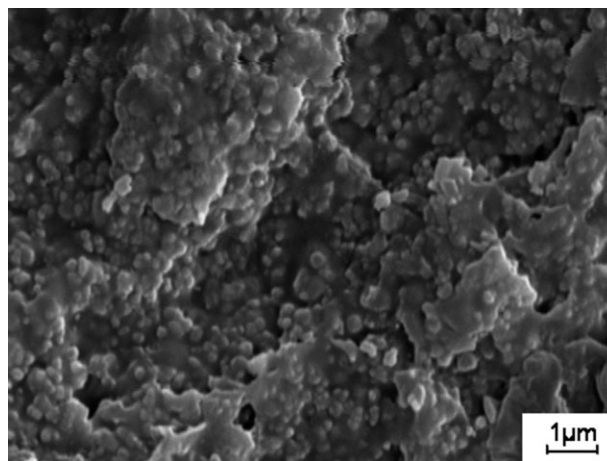


Figure 6 The SEM image of coating containing chrome oxide/M100 pigment at a pvc of 50%.

using data concerning surface characteristics, obtained by the IGC technique.

The decrease in the mechanical properties beyond the maximum peak is attributed to the two possible causes, aggregate formation, and void introduction. For the systems containing pigment chrome oxide/M100, the relative ultimate tensile strength decreased immediately, relative to the nonpigmented equivalent, when the chrome oxide pigment was introduced into the coating system. This performance was rationalized by the small value of γ_s^d related to the pigment chrome oxide/M100 and also its inferior degree of dispersion.

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