SCRATCH AND MAR RESISTANCE OF POLYMERIC MATERIALS

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Abstract

Scratch and mar resistance is an important characteristic for polymeric material systems in numerous applications. However, important links between material properties and scratch resistance remain illusive. Thus, optimization of material properties is not yet possible for applications in which scratch resistance is important. Further progress in this area will require the development of an advanced methodology incorporating improved measurement techniques and more appropriate models that include time-dependent behavior and realistic stress states. Studies to date have typically lacked systematic variation of important test variables, and often have included only a single material or a limited set of similar materials. Current scratch test methods differ widely in many aspects, making studies difficult to compare. Also, current test methods lack reliable criteria for determining which materials will truly exhibit better mar resistance in service. This failing is related to the lack of appropriate appearance measurements as related to scratch and mar resistance. In this paper, literature is reviewed in which scratch and mar resistance of polymeric materials is reported. This review includes discussions of various instrumented scratch testing devices and methods, evidence for relationships between various material properties and scratch resistance, and appearance issues.

Introduction

The need to quantify the scratch and mar resistance of polymeric materials has led to the development of numerous test methods, some standardized through groups such as the American Society for Testing and Materials (ASTM), some standardized within particular companies, and others that have not been standardized. The large number of test methods has particularly affected commerce between material suppliers and end users. For example, each automotive company generally has a different test method and specification related to scratch and mar, such that a materials company must perform each of these tests for any polymeric system that it supplies for automotive applications for which good appearance is a key attribute. Entrance of a polymeric material into multiple markets often requires different sets of scratch and mar resistance tests for each market. The time and costs associated with performing the many different scratch and mar resistance tests are significant, and whether any of the tests yield reliable results regarding the in-service performance of a material remains an unanswered question.

Surface mechanical testing of polymeric materials, including indentation and hardness tests and tests of scratch and mar resistance, have been used with limited success and primarily for qualitative comparisons and quality control. Published accounts can be found as early as the 1950s [1, 2]. In terms of scratch and mar resistance, tests have been developed based on service conditions that can cause scratching and marring of a polymer [3-11]. These field simulation tests generally perform either wet abrasion using abrasive slurries or dry abrasion using abrasive powders or papers. For example, laboratory-scale instruments have been developed to simulate car wash conditions for qualifying mar resistance of automotive coatings. Although more of a wear test, the Taber abrasion test is often used for plastics and occasionally for coatings, in which samples are rotated under weighted abrasion wheels [11-16]. All of these types of tests produce relative measures of scratch resistance, usually based on mass loss, visual inspection, gloss changes, or changes in gray scale level or ΔL, often with poor repeatability and/or reproducibility. To produce measurable changes in such metrics, the severity of these tests in terms of applied force or length of test, for example, can be high such that damage mechanisms deviate from in-service conditions and misleading results are produced [17].

More recent efforts have been aimed at measuring quantitative material properties and understanding relationships between surface properties and performance characteristics. In most of these studies, single-probe testing devices [6-8, 17-52], including depth-sensing indentation and scratch systems [6, 7, 17, 36-43] and atomic force microscopes [8, 44-52], have been used. These types of tests attempt to simulate single asperity contact, as opposed to multi-asperity contact associated with the field simulation tests. Single-probe scratch testing can be useful for characterizing polymeric materials under a number of contact conditions, particularly because it is a controlled dynamic process which is suitable for characterizing time and strain dependent behavior [20]. As previously discussed, field simulation testing has been labeled as too severe in some cases relative to service conditions. However, similar criticism of single-probe testing can be found. Such criticism is related to unclear terminology regarding the definitions of marring and scratching. In general, marring occurs under less severe conditions compared to scratching, and the dimensions or mars are less than those of scratches. Prior to the use of sensitive depth-sensing systems and atomic force microscopes, typical single-stylus tests produced scratches that were more severe than marring damage observed in service conditions [13]. As will be discussed, even with the depth-sensing systems, inadequate choices of tip geometry and loading conditions can still produce scratches that are much larger than typical mars [6].

Perhaps the distinction between scratching and marring is best related to appearance attributes. For example, marring is often associated with a high density of small, shallow scratches distributed over a relatively large area such that larger scale appearance attributes (e.g., gloss or distinctness of image) are affected. Scratching, on the other hand, can be associated with a much lower density of larger, deeper scratches, sometimes even single scratches, where the extent of the scratch dimensions is related to the ability of the customer to perceive the scratch. Currently, relationships between appearance attributes and surface deformation associated with scratching and marring are poorly understood. This lack of understanding is one of the major barriers to the development and acceptance of standard measurement techniques for determining scratch and mar resistance.

Another major barrier to the development of a unified standard or set of standards for determining scratch and mar resistance is the specification of testing conditions. Even among the relatively similar single-probe devices currently being used, test variables, such as tip geometry, scratch speed, and applied load, differ from one study to another, sometimes by orders of magnitude. Because scratch and mar behavior is related not only to the surface properties of the material but also to the associated loading conditions, laboratory testing should provide an understanding of how the material will perform under a wide variety of conditions. In particular, temperature and rate effects should be accounted for whenever polymeric materials are involved due to the rate and temperature dependence of polymer properties. Further, the important rates that must be considered are the rates of change of the local stress and strain fields, which are related to the rate dependent material properties, the probe geometry, the loading rate, and the scratch speed. To date, only Briscoe and coworkers [19-28, 43], and to a lesser extent Sue and coworkers [33-36], have provided studies in which either the effects of different test variables were systematically investigated or polymers with widely varying properties were subjected to the same scratching conditions. Also, very little modeling has been performed to understand how changes in testing conditions affect the local stress and strain fields. Because of these deficiencies, relationships between polymer properties and scratch and mar resistance are poorly understood.

In this paper, published studies involving scratch and mar resistance testing of polymers are reviewed. In this review, testing systems are described and discussed, with an emphasis on the single-probe testing systems. Current understanding regarding relationships between scratch and mar resistance and between material properties and appearance attributes is then reviewed. Recommendations are then made regarding future test method development.

Scratch Testing Systems[1]

Dedicated Single-Probe Scratching Systems

Recent developments of dedicated single-probe scratching systems include efforts to improve upon ASTM D 5178: Standard Test Method for Mar Resistance of Organic Coatings [18]. In this test method, polymeric coatings are scratched with a single "U-shaped" stylus at a speed of 6 mm/s over a minimum distance of 75 mm. The stylus is a bent 1.6 mm diameter rod of either chromium-plated, nickel-plated, or heat-treated polished steel, with the "U" having an outer diameter of 3.25 mm. The surface finish of the stylus, the surface preparation of the coating, and the coating thickness are not specified but must be reported. The applied load, not to exceed 98 N, is successively increased or decreased in an attempt to determine the minimum critical load at which marring occurs. Note that mar resistance in this method is defined as the ability of a coating, under conditions of light abrasion, to resist damage. Whether or not damage occurs is qualified by visual inspection under unspecified conditions. Once the critical load is

[1] Certain commercial instruments and materials are identified in this paper to adequately describe the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the instruments or materials are necessarily the best available for the purpose.

determined, the test is repeated five times at each of three loads: just above the critical load, just below the critical load, and at the critical load, with the three different loads applied randomly. For each load, the number of times marring occurred is tabulated and reported.

Attempts to improve upon this test have resulted in several other test devices and methods, for example the Ford Laboratory Test Method BN 108-13 [8, 32-36] and progressive load test methods [17, 36-43] as well as both commercial and non-commercial stylus scratch devices with varying levels of automation [19-31]. Similar to ASTM D 5178, the Ford test is a constant load scratch method utilizing single-probe loading. However, in order to test a range of loads simultaneously, five separate probes are utilized, each applying a different constant load to the polymer. Typically, loads of 0.6 N, 2 N, 3 N, 6 N, and 7 N are applied for polymeric coatings [8, 32-34] while applied loads up to 30 N have been reported for thermoplastic polymers [35, 36]. The probes are 1 mm diameter polished steel spheres and the scratch speed is 100 mm/s. The scratch length is generally not reported but is likely to be on the order of 10 mm. Scratch resistance is defined by the residual scratch depth as measured using an optical interferometer with 5X magnification at some period of time, often 24 h, after scratching. However, Ryntz et al. reported that the amount of recovery of model automotive coatings could change significantly between 24 h and 720 h (30 d) after scratching [8]. Such recovery typically occurs only in the direction normal to the surface and can be enhanced by elevated temperature exposure, such as occurs when an automotive coating sits in the sun on a warm day [17]. Further, in the case of automotive applications for which this test is typically used, interior and exterior polymer coatings and plastics are exposed to a wide range of temperatures, which will drastically affect the rates and perhaps even the amounts of recovery, as well as the actual deformation mechanisms.

To determine critical loads related to scratch and mar resistance from a single scratch, progressive load testing has been developed, in which the applied normal force is increased at a constant rate from some minimal force value up to a predefined maximum force. Unlike the ASTM D 5178 and Ford test methods, devices that can perform progressive load tests (see next subsection) typically allow the frictional forces and penetration depths to be measured during the scratching event. Thus, a friction coefficient can be determined for the particular probe-material combination. Further, profilometry is often performed before and after scratching, such that the penetration depth information can be compared to the initial slope and/or texture of the surface as well as the residual deformation. Optical microscopy or atomic force microscopy can be used to further evaluate the damage mechanisms with respect to the corresponding loads. In the case of polymer coatings, critical loads corresponding to changes in damage mechanisms are often observed. However, relationships between these critical loads and appearance attributes have not been quantified. Also, for many polymers, particularly thermoplastic materials, abrupt changes in damage mechanisms are not observed, such that critical loads cannot be defined [36]. Finally, the wide range of test variables found in published progressive load scratch studies renders the comparison of one study to another extremely difficult. These differences will be discussed further in the next subsection.

Depth-Sensing Systems

Depth-sensing indentation systems, sometimes referred to as nanoindenters, have become useful tools for measuring local mechanical behavior at the micrometer and even sub-micrometer length scales [53]. One of the most significant differences between studies using depth-sensing systems and those using the dedicated scratching systems described previously is the use of sharp pyramidal probes with tip radii less than 100 nm. From a tribological standpoint, these sharp probes allow studies that are closely related to single asperity contact [19]. However, as will be discussed, the contact stresses will be significantly different compared to the larger probes normally associated with dedicated scratch systems. Several commercially available systems offer capabilities to perform indentation and scratch testing of materials [6, 17, 36-39, 43]. In terms of scratch testing, robust feedback systems allow for specification and control over several important testing parameters, including the applied normal force, the scratch length, and the scratch speed. Typically, either constant load scratch testing or progressive load scratch testing is performed. In the former, a specified normal force is held constant over the length of the scratch, whereas in the latter, the load is linearly increased from a specified initial force to a specified final force.

As mentioned previously, test variables can vary significantly between published studies involving scratch and mar resistance testing with dedicated scratch and depth-sensing systems. Probe tips can include diamond or steel spheres [8, 32-36], conical diamond probes [40-42], and cube-corner [17] and Berkovich diamond pyramids [17, 29]. Also, the geometric aspects of these probes, such as tip radius and relevant angles, can vary significantly from one study to another, as shown in Table 1. Each type of tip geometry is associated with a different complex stress state, which in general will be quite different from stress states that create scratches and mars on products during production, shipping and handling, or service. Scratch speeds also vary widely, from 100 mm/s for the Ford test [8, 32-36] down to 5 μm/s for a progressive load study [38]. For progressive load tests, loading rates can also vary from 0.02 mN/s [42] up to 1 N/s [36]. In general, scratch speeds and loading rates (where applicable) have been higher for larger tip radius probes and lower for smaller tip radius probes.

While variations in scratch test parameters makes comparisons between studies difficult, many published studies are missing key information regarding important scratch test variables (e.g., tip geometry, scratch speed, loading rates, and minimum and maximum loads). All of these variables affect the contact stresses and strains and thus the damage modes [20]. For example, as the probe attack angle increases or as the normal force increases, contact stresses increase resulting in increased damage and potential changes in damage modes [17, 19-26]. For a given polymer, similar damage modes could be observed for a smaller spherical probe applying a relatively small normal force compared to a larger spherical probe applying a larger normal force, assuming all other test parameters are the same. Such similarity can occur because of the similarities in the ratio of contact radius to probe radius, which as will be discussed is related to the contact strain. Unfortunately, faster scratch speeds have generally been used in studies in which larger probes are used. Increased scratch speed, however, can cause an increase in adiabatic frictional effects, causing local heating and suppressing brittle behavior [19]. Therefore, at a minimum, standardization of these types of test methods should include the reporting of all key test parameters with perhaps some limitations on the allowable ranges of these parameters.

The ratio of friction force to normal force in a scratch test, sometimes referred to as a friction coefficient, is a strong function of the contact geometry as well as the scratch rate, the probe material, and the polymer, and is affected by surface lubrication [19-23]. It is also a function of the penetration depth and damage behavior [19-23, 36, 40-42]. Some research indicates that friction coefficient does not impact significantly the scratch and mar resistance of polymeric materials, while other studies suggest otherwise [13]. Thus its significance as a material parameter is not clear. As will be discussed, friction force and hence friction coefficient appear to be related to the net energy dissipated or work done during the scratching process, and thus are related to the damage mechanisms that occur during scratching.

Table 1 Comparison of some important test variables used in single-probe scratch and mar resistance studies reported in the literature.

Test	Tip Material	Tip Geometry	Load Range	Speed	References
ASTM D 5178	Steel	"U"-shaped loop 3.25 mm diameter	0 N - 98 N	6 mm/s	18
AFM	Diamond	90° cone 1 μm or 1 mm radius	50 μN - 4 mN	(35-70) μm/s	8, 44, 45
Ford	Steel	sphere 500 μm radius	(0.6 - 30) N	100 mm/s	8, 32-36
Constant Load	Diamond	Berkovich pyramid < 0.1 μm radius	(1 – 7) N	500 μm/s	29
Progressive Load	Diamond	sphere 2 μm radius	(0 - 5) mN	5 μm/s	38
Progressive Load	Diamond	sphere 200 μm radius	(0.5 – 10) N	200 μm/s	38
Progressive Load	Diamond	sphere 10 μm radius	(0 – 190) mN	50 μm/s	6, 39
Progressive Load	Diamond	60° cone (1-3) μm radius	(0 – 8) mN	25 μm/s	40-42
Progressive Load	Diamond	Berkovich pyramid < 0.1 μm radius	(0.02 – 16) mN	(10-25) μm/s	17
Progressive Load	Diamond	cube corner pyramid (0.5-2) μm radius	(0.02 – 16) mN	25 μm/s	17

Scanning Probe Microscopes

Scanning probe microscopes, for example, the atomic force microscope or AFM, have also been used to perform scratch testing of polymeric materials [44-52]. In general, however, scratch test data taken with an AFM will be qualitative at best. This disadvantage arises because of a lack of force feedback during AFM force mode operation, in which indentation and scratch testing is often performed. During force mode, instead of scanning the probe laterally across the sample, the probe is positioned above a single area and moved vertically. The tip deflection, which is proportional to the force and is measured with an optical lever detection system, is plotted as a function of the motion of the piezoelectric scanner in the z direction to produce a force curve. During a scratch test, the probe tip moves toward the sample, contacts and penetrates into the sample surface, moves laterally across the sample, and then lifts off of the sample surface. The corresponding force curve provides information regarding the initial loading prior to the scratch and the unloading after the scratch has been made.

Because the scratch test is made with a probe at a fixed vertical position with respect to the sample, a material exhibiting time-dependent behavior will undergo a stress relaxation process so that the actual applied force decreases over the length of the scratch. This behavior is shown in Figure 1. In this figure, force curves are shown for three different epoxy samples with glass transition temperatures, T_g, ranging from approximately 13 °C up to 150 °C, as measured by differential scanning calorimetry. For the lowest T_g epoxy, Figure 1c, the difference between the maximum tip deflection for loading and that for unloading is large compared to the other two epoxies, which have T_g values of 68 °C (Figure 1b) and 150 °C (Figure 1a), respectively. Thus, because of the lack of force control, scratch tests performed on polymers with the AFM will have a non-uniform force history. Further, no capability exists to vary the load in a controlled manner over the length of the scratch, such as is done with the progressive load test discussed previously.

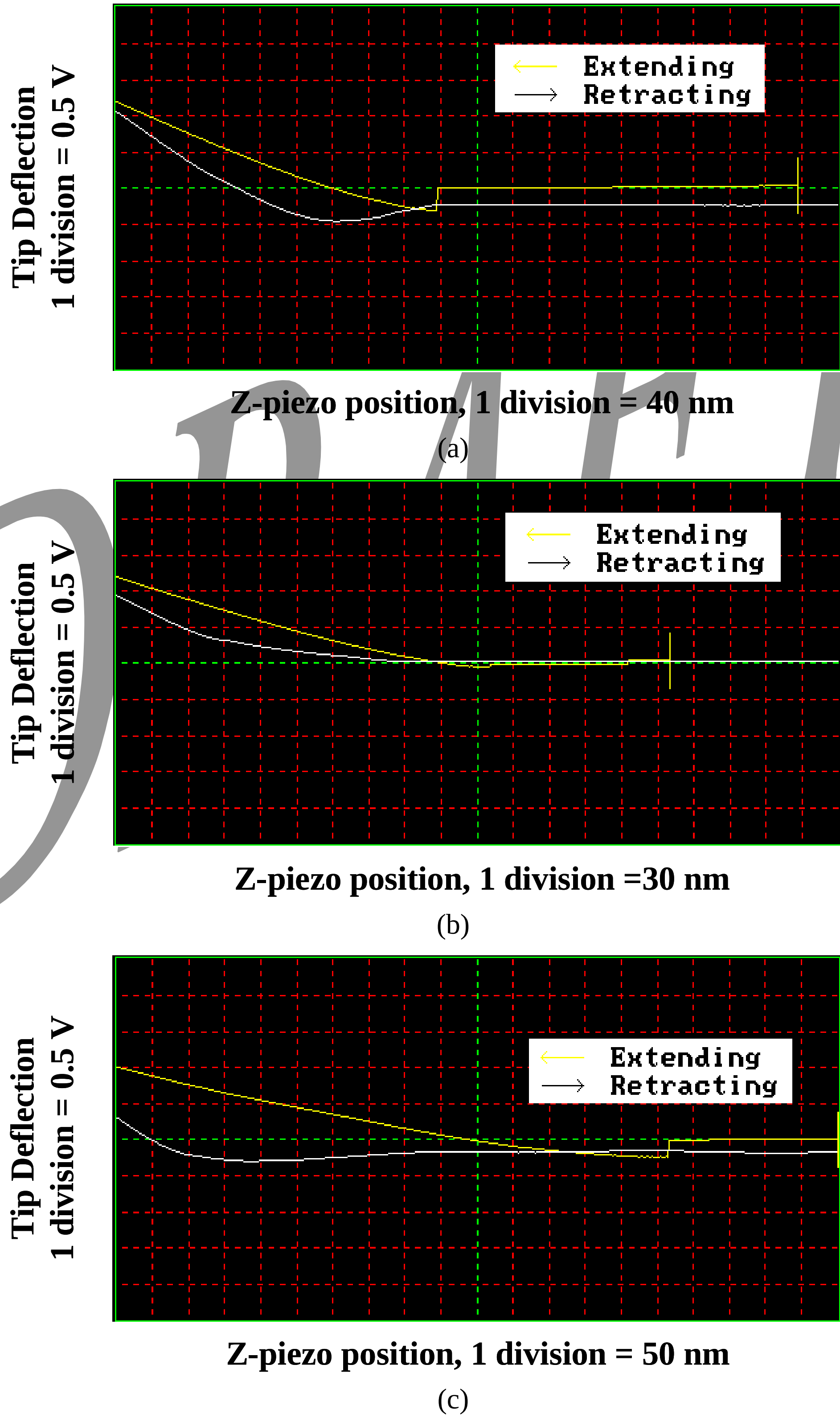

Figure 1 AFM force-distance plots related to 90° scratch tests on three epoxy materials with T_g values of 150 °C, 68 °C, and 13 °C in (a), (b), and (c), respectively.

Another disadvantage of using the AFM for scratch testing is related to the measurement of tip-sample forces during scratching. In general, AFM systems do not provide a measurement of tip-sample forces during the scratch. Again, the force curve only contains force data taken prior to and after scratching. Potentially, the photodiode signal, which gives a measure of the tip-sample forces, could be accessed with enhanced data acquisition capabilities, for example, a signal access board and a secondary acquisition computer. However, AFM scratch tests are normally preformed with the lateral motion of the probe tip perpendicular to the cantilever probe's neutral axis, sometimes referred to as a 90° scratch test. Thus, the lateral friction forces act on the tip in such a way that the cantilever probe twists. While methods for measuring the bending-mode spring constant of AFM cantilever probes have been developed, no methods for quantifying the lateral (twisting-mode) spring constant currently exist. Therefore, even if tip-sample forces were acquired during scratching, calculating the corresponding frictional forces would not be possible. Also, bending and twisting of the cantilever can both occur during scratch testing, creating further problems with measuring and controlling tip-sample forces.

In an attempt to overcome these difficulties, Du et al. [52] performed 0° scratch tests, pulling the tip across the surface such that the lateral motion of the probe tip was parallel to the cantilever probe axis. In this case, the friction force increases the bending of the probe from that caused by only the normal or indentation force. Using appropriate free body diagrams of the probe, the difference in the maximum force between loading and unloading measured from the force curve was used along with the bending-mode spring constant to calculate the friction force. Again, however, no data was taken during scratching and because of the lack of force control, stress relaxation effects, which decrease the normal force after scratching relative to that applied prior to scratching, compete with the increase in probe bending caused by the friction forces in a

0° scratch test. In Figure 2, a set of force curves is shown for the lowest T_g epoxy for 0° scratch tests at two scratch rates. The scratch rate corresponding to Figure 2b is 5 times that of Figure 2a, such that stress relaxation effects are reduced. For the slower scratch rate (Figure 2a), stress relaxation dominates such that the bending deflection of the probe is lower after scratching than before scratching. However, for the faster scratch rate (Figure 2b), the probe deflection for unloading is larger than that for loading, indicating that stress relaxation effects were substantially reduced.

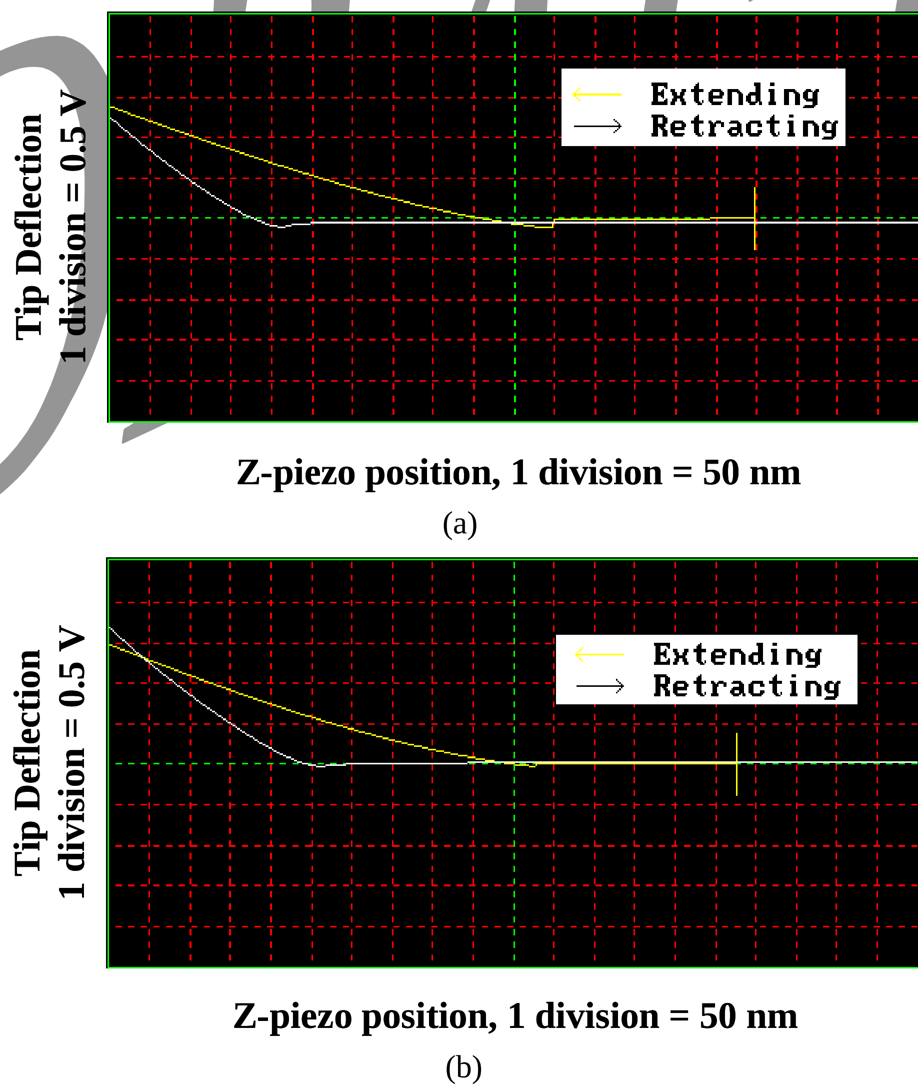

Figure 2   AFM force-distance plots related to 0° scratch tests for the epoxy material with T_g = 13 °C. The scratch rate corresponding to (b) was 5 times that corresponding to (a).

Other disadvantages of using AFM systems for scratch testing include: (1) a lack of information regarding the tip shape, which generally deviates significantly from ideal tip shapes; (2) nonlinearities and cross talk problems associated with the piezoelectric scanners and the optical lever system; (3) limited load, depth, and scratch length capabilities; and (4) a lack of developed analysis software. While an approach to measure the tip shape of AFM probes used for indentation measurements has recently been reported [54], no efforts to address the many other limitations of scratch testing using AFM cantilever probes are currently being pursued.

Despite these limitations, however, Jones and coworkers [44-51] have reported a number of scratch testing studies of polymeric materials in which an AFM, which was modified to provide force feedback during scratching, was utilized. In these studies, cross-sectional analysis of the damage created during scratching was used to provide a measurement of so-called micro-mar resistance (MMR), defined as the normal force divided by the cross-sectional area between the two shoulders on either side of the ditch (see Figure 3). Also, estimates of the relative amounts of elastic recovery, plastic deformation, and fracture during scratching were calculated using appropriate ratios of the areas defined in this cross-sectional analysis. Areas measured or estimated include those of the indentation at maximum load and the ditch and shoulders remaining after scratching. The appearance of shoulders was assumed to be an indication of plastic deformation, while the lack of shoulders remaining after a scratch was an indication that fracture dominated the scratch process. In some studies, images of scratched regions taken at different times after scratching were used to estimate long-term viscoelastic recovery of scratches for various polymers [44, 48].

Initially, diamond shards were glued to tungsten cantilevers to create scratch probes [44, 46-50]. More recently, however, a manufactured diamond conical probe has been used in place of the diamond shards [8, 45, 51], presumably for improved repeatability of tip geometry and for comparisons with other single-probe scratch tests. Even with the improvements made, the level of quantitation of this method is not sufficient for measuring scratch and mar resistance. The relative amounts of elastic, plastic, and fracture deformations change with force, and thus so does MMR. Because data is only obtained after scratching, samples that exhibit a lot of recovery under the particular scratching conditions used have high values of MMR. To date, criteria for using MMR to predict the relative scratch and mar resistance of polymers in service has not been provided.

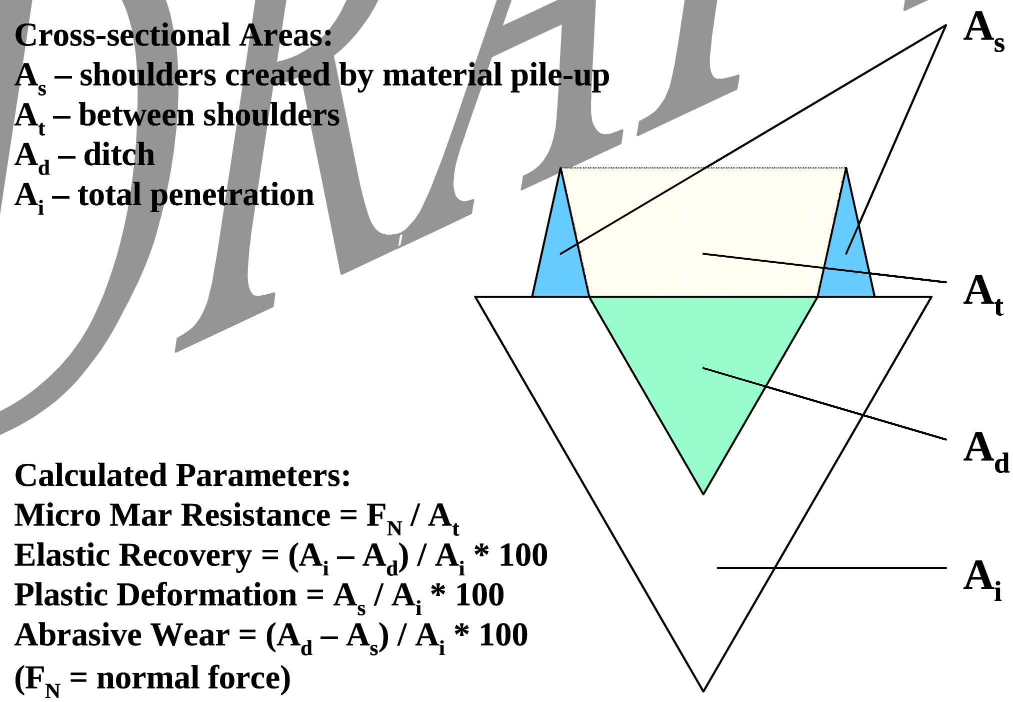

Figure 3 Illustration of analysis used by Jones and coworkers [44-51] for AFM scratch testing.

Field Simulation Systems

Several types of systems have been designed to simulate situations that occur in service that cause scratching and/or marring of polymeric material systems. Some of these devices are instrumented to provide force and displacement measurements while others produce scratches and mars through some mechanical interaction with a sample surface, which is characterized before and after scratching using various methods, such as gloss measurement. The most common of these field simulation methods are a laboratory-scale car wash and a rubbing method adapted from the testing of textiles [6]. In these methods, wet abrasive slurry or a dry powder is applied to the polymer surface under normal and lateral forces using a brush or felt pad [5-11].

These techniques have at least the potential advantage of being somewhat closely related to field conditions of interest. Reportedly, the "standard" source of scratch and mar damage for exterior automotive coatings is car washing [55]. However, the mechanics (forces, stresses, strains, etc.) associated with these tests are complex, such that relating the resulting damage to material properties is generally not possible. Also, as will be discussed, the effects of such "standard" damage on coating appearance are yet to be quantified, and determining scratch and mar resistance using field simulation testing is often based on visual inspection or measured changes in gloss or gray level. However, these appearance techniques are generally inadequate for characterizing surface texture and defect structures such as those associated with scratch and mar behavior. Thus, the use of these tests in evaluating scratch and mar resistance is limited.

Qualitative Assessment of Scratch Performance

Scratch Maps

While acknowledging the importance of establishing property-performance relationships for scratch and mar resistance, most studies have focused on scratch morphology and damage mechanisms, in particular scratch size (depth and width) and whether scratch damage is characterized by elastic, viscoelastic, plastic, or brittle deformation or a combination thereof. The goal of these studies is often to link the damage processes and associated geometry to the mechanical dissipation properties of the material. The most extensive work on this topic has been by Briscoe and coworkers, who have developed scratch maps to relate scratch deformation modes to contact conditions [19-27]. In these studies, single-probe scratch testing was performed with conical shaped probes. The primary external variables that were controlled included cone angle, applied load, sliding velocity, and the state of interfacial lubrication. Control over load allowed changes in damage mode to be studied as a function of penetration depth. Changes in penetration depth were believed to be related to strain density, while contact strain was assumed to dependent primarily on cone angle. The presence of interfacial lubrication primarily acted to suppress brittle cracking. Increasing scratch velocity also suppressed brittle cracking, possibly because of heat generated due to adiabatic frictional loading. In fact, scratch rate was found to be the most significant variable affecting the scratch behavior of polymers [19, 20]. In another study, increasing the sliding speed resulted in thinner residual scratches [17].

A scratch map can be developed by the systematic variation of two variables and the qualitative determination of the resulting deformation mechanisms. Because elastic, plastic, and viscous responses and the ductile-to-brittle transition for polymers are highly strain dependent, cone angle was often used as one of the variables, often along with applied load. Different types of maps were also created by plotting friction coefficient or scratch hardness as a function of cone angle, for example, often for different scratch velocities and with the resulting deformation mechanisms identified.

One of the primary conclusions of these mapping studies is that polymers exhibit a wide range of deformation modes, much wider than metals and ceramics, within a relatively narrow range of contact variables [20, 28]. However, scratch maps do not provide all the information needed to evaluate damage under all conditions, and the scratch hardness, which is related to the scratch width, is typically the only measurement used to evaluate scratch resistance.

Relationships between scratch deformation and appearance must be determined to enhance the use of scratch maps for evaluating scratch and mar resistance of polymeric materials.

Scratch Damage Mechanisms

In general, deformation during single-probe scratch testing of a polymeric material progresses as a function of the severity of contact conditions from elastic deformation to a smoothing of local asperities called "ironing" to viscoelastic-plastic ploughing, followed by crack formation in or at the edges of the scratch groove and then by even more severe types of deformation. For amorphous thermoplastics, such as poly(methyl methacrylate) (PMMA), severe deformation is usually brittle deformation without plastic flow that includes chipping of the material and is sometimes called "machining." For semicrystalline polymers, such as high-density polyethylene (HDPE), the initial cracking is often regularly spaced along the scratch groove, with the formation of viscoelastic "waves" and finally "cutting" of the polymer, which is a deep grooving process with cracking due to tearing [20], occurring under increasingly severe contact conditions. These deformation processes are highly dependent on contact geometry and, to a lesser extent, penetration depth. Increasing temperature enhances viscoelastic and plastic ploughing responses while decreasing the tendencies for elastic and brittle responses.

Scratch damage for different polymers has often been compared under a given set of scratch test conditions. For example, under progressive load testing with normal load ramped from 0 N to 30 N at a rate of approximately 1 N/s, greater than 70% recovery of the scratch penetration depth was observed over the entire load range for low density polyethylene (LDPE), HDPE, PP, poly(ethylene terephthalate) (PET), Nylon 6,6, and Nylon 6,6 blends, one with mica and one with rubber [36]. A 50 μm diameter diamond sphere was used with a scratching speed of 20 mm/min. In the same study but using a 30 N constant load with the Ford test device, brittle fracture was observed for polystyrene (PS) while ductile ploughing was observed for polycarbonate (PC) [36]. In another study, ductile ploughing was also observed for PC under a 3 mN constant load, a 2 μm radius diamond sphere, and a sliding speed of 0.3 mm/min [38].

For both amorphous and thermoplastic polymers, combinations of ductile ploughing (i.e., formation of a scratch groove) and cracks or "ripple marks" on the bottom of the scratch groove, often extending to the edge of the groove, have been reported [17, 33]. As discussed previously, however, scratch damage is extremely dependent on contact geometry, as well as other testing variables. Scratch damage appears to be particularly dependent on the attack angle of the probe, which is related to the contact strain, with higher attack angles producing increasingly brittle damage modes [17, 20]. In a study using pyramidal probes, attack angles between 30° and 40° caused cracking in a set of automotive clear coatings [17]. An important measurement issue to then consider is how attack angle or contact strain changes as a function of penetration depth for a given tip. Such considerations should include tip defects, produced either in fabricating the tip or in the use of the tip, and the ability to fabricate tip shapes in a reproducible manner, both of which may limit the choice of material and tip geometry in a standardized test method.

Quantitative Interpretation and Modeling of Scratch and Mar Resistance

As has been discussed, a number of studies have shown the pronounced influence on scratch resistance that the contact geometry has in single-probe tests [17, 19-27]. In one of these studies [20], the ratio of elastic modulus, E, to yield stress, Y, was combined with a geometric parameter related to the contact strain, e.g., tan θ for probes with geometric similarity (conical and pyramidal geometries) and r/R for spherical probes, to compare the scratch behavior of different polymers. Here, θ is the effective cone or attack angle, and r is the contact radius for a spherical probe of radius R. Plotting the friction coefficient as a function of these parameters results in an observed threshold in (tanθ)(E/Y) and (r/R)(E/Y), below which only elastic deformation and "ironing" occur. In this region of the plot, the friction coefficient was relatively constant and close to the value of the pressure coefficient of interfacial shear stress. Above this threshold value, viscoelastic and plastic ploughing occur followed by brittle deformation processes, and the friction coefficient increases with increasing values of (tanθ)(E/Y) and (r/R)(E/Y). These trends reflect the relationship of the friction force, and hence friction coefficient, to the net energy dissipated or work done during the scratching process [20].

Scratch hardness has been defined and used in an analogous manner to indentation hardness, i.e., as the applied normal load, P, divided by the projected area supporting the normal load:

$$H_s = q \frac{P}{\pi/4 \, w^2} \tag{1}$$

where w is width of the scratch groove. Unlike during indentation, the probe is fully supported only on its front side, and the amount of support on the back portion is dependent on the amount of recovered material. The non-dimensional parameter, q, accounts for this difference. Its magnitude ranges between 1 and 2 and depends on the relaxation response of the material. For a material and contact conditions for which deformation is either not recovered or recovers very slowly with respect to the time scale of the scratching motion, the area supporting P is roughly half that compared to the indentation case, and thus q approaches 2. For a material and contact conditions for which deformation is recovered very quickly with respect to the time scale of the scratching motion, q approaches 1. Further, generally larger amounts of recovery have been associated with higher scratch resistance because the residual scratch depth is reduced. For identical scratching conditions that create the same penetration depth and hence scratch width in two materials, the scratch hardness value would be lower for the material exhibiting more significant recovery over short time scales compared to the other material. However, q has been used only in an empirical sense, and no attempts have been made thus far to relate q to material properties or even to differentiate between the scratch hardness of two different polymers.

Jardret, et al. [29] argued that perhaps a more appropriate definition of scratch hardness would consider not just the residual scratch width but the actual contact area during the scratch test, which is related to the contact depth through the indenter geometry. By comparing the contact geometry during scratching to the residual scratch geometry for two polymers and three metals, the relative amounts of elastic and plastic deformation correlated to the ratio of E to indentation hardness, H. In this study, a Berkovich tip with the edge facing the scratch direction was used at a penetration depth of 50 μm and a speed of 500 μm/s. Empirical relationships were also observed between the ratio of contact depth to penetration depth and (tanθ)(E/Y) as well as to (E/H) [29]. Note that H can be proportional to Y for many materials, and the ratio E/H has also been found to be an important parameter in indentation testing [20]. Finally, using estimations of contact depth and height of the material pile-up in front of the probe, the estimated average mean pressure on the front faces of the Berkovich indenter during scratching was similar to values of Vickers hardness for the different materials [29].

The majority of sliding contact models typically have been used to study friction, wear, and machining behavior of metals. Because many of these models are numerical (e.g., finite element) models that are specific to a particular type of process, little information can be gained from these studies regarding scratch and mar resistance of polymers. Analytical models that are relevant to scratch and mar resistance include that of Hamilton and Goodman [56] and those discussed by Williams [57]. The Hamilton and Goodman model is based on sliding contact between a spherical probe and a flat, elastic surface and is valid for small penetration depths relative to the probe radius. In fact, the motivation for this model was to understand measurements of frictional properties of material surfaces in which a spherical slider was moved across a flat surface under small normal loads. According to this model, significant surface tensile stresses are generated at the trailing edge of contact during such sliding, the magnitude of which depends on the friction coefficient; the higher the friction coefficient, the larger the tensile stress. Using the von Mises yield criterion, the model also was able to predict surface yielding, which intensifies as the friction coefficient increases.

While the analytical models discussed by Williams [57] were developed with metals as the materials of interest, the models focused on indentation and scratch behavior with respect to test methods often used for quality control. These models utilize two hardness parameters, the so-called scratch hardness, H_s, defined similarly to Equation (1), and the ploughing hardness, H_p, defined as

$$H_p = \frac{F}{A_p} \qquad (2)$$

where F is the tangential or friction force and A_p is the projected area of material in contact with the leading edge of the probe. This second hardness value is related to the energy required to displace a unit volume of material. Often in the case of a hard probe scratching a soft surface as is the case in the scratching of polymers, material is both displaced and also physically detached from the surface. For soft metal surfaces, the physical detachment process only occurs for attack angles above a critical value, an observation that appears to be consistent with polymer scratch literature [17, 20].

The simplest model of friction during a scratch test leads to an expression of the friction force, F, as the sum of the adhesion and ploughing friction forces, F_A and F_P, respectively. The adhesion term is related to the state of surface lubrication and the ploughing term is a function of the probe geometry. Because this model is based on equilibrium, however, it lacks information regarding the relative magnitudes of the normal and frictional forces or the geometry of the deformed material. Because scratching is inherently three-dimensional, more advanced models have either been three-dimensional, using the Upper Bound method, or two-dimensional, in which case the solution is extended to the third dimension through various arguments. However, these models are for elastic-plastic materials and do not account for viscoelastic behavior.

A well accepted view of deformation local to an indentation by a rigid conical or pyramidal probe is shown in Figure 4 [57]. Immediately under the region of contact is a region of high stresses. In fact, for an ideal (non-rounded) probe tip, stress is infinite at the apex of the indenter. However, the maximum shear stress within the material is finite and equal to $E(\tan\theta) / \pi$, where θ is the attack angle of the probe with respect to the sample. For a given material, limiting values of load and attack angle exist below which the material can respond elastically and beyond which a plastic region is formed that is then surrounded by an elastic hinterland. Thus, yielding occurs when $E(\tan\theta) / \pi$ is equal to the shear yield stress, which is in turn proportional to the tensile yield stress, Y. Further, the indentation pressure also is related to $E(\tan\theta) / Y$, again showing the importance of this collection of parameters, as was noted by Briscoe [20]. This grouping can be thought of as the ratio of the strain imposed to the maximum strain that can be sustained by the material prior to yielding.

In terms of fracture, as determined by Hamilton and Goodman [56], a maximum tensile stress on the surface is generated at the trailing edge of the contact area during sliding or scratching. This stress can generate cracking. However, localized plasticity will reduce the magnitude of the tensile stress and can shift its location to below the surface potentially causing subsurface cracking [57], as has been observed in some polymer systems [36]. As the probe moves across the surface, families of cracks can form, which has been attributed to a mismatch between strains in the plastic region and those in the elastic hinterland, causing residual tensile stresses in the material [57]. Thus, the competition between plastic deformation and fracture during a scratch test is complex, making predictions of material behavior difficult. Currently, no complete model of the scratching process has been developed.

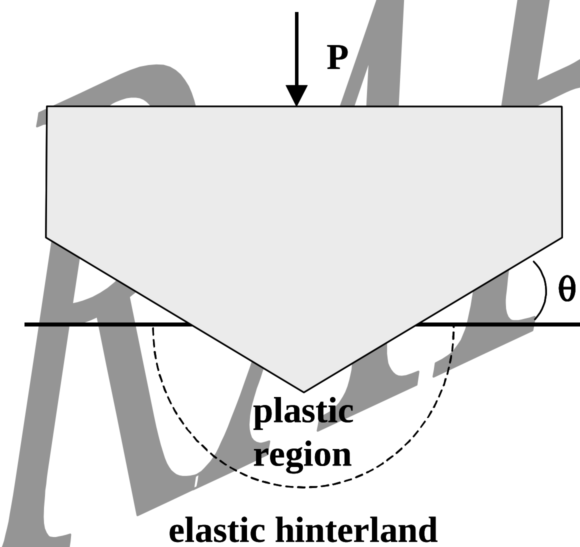

Figure 4 Illustration of the indentation of an elastic-plastic material by a conical or pyramidal indenter with an attack angle, θ.

Property-Performance Relationships

Except for a few studies in which certain scratch variables have been studied systematically, the objectives of scratch and mar resistance studies of polymers have typically fallen into one of the following categories: (1) determine a relative ranking of similar materials; or (2) determine scratch behavior under a specified set of test conditions for a single material or set of similar materials. In either case, the results depend on the type of test and how scratch and mar resistance is determined. In Table 2, a summary of popular test methods is given along with the corresponding measure of scratch and/or mar resistance, the associated method of measurement, and any criteria used to help guide the measurement. Note the significant lack of similarity between the various tests. Further, in very few published studies are the tests performed under the same scratching conditions (see for example Table 1), and even fewer studies have included polymers that have significantly different chemical structures and properties. These shortcomings have thus limited the determination of relationships between various properties and scratch and mar resistance.

Table 2 Comparison of scratch and mar resistance test methods in terms of how scratch and/or mar resistance is measured, the method used for such measurement, and any associated criteria for the measurement.

Test	**Measure of Scratch/Mar Resistance**	**Method**	**Criteria**
ASTM D 5178	Critical Load	Visual Inspection	None
ASTM D 6279	Change in Gloss	20° Gloss with Glossmeter	ASTM D 523
Ford	Residual Scratch Depth	Optical Interferometry 5X Magnification	Measured 24 h After scratching
AFM	Micro Mar Resistance	Calculated (see Figure 3)	Area measured from AFM
Progressive Load	Critical Load	Measurements Of Lateral Force	Transitions in Data

Despite the lack of rigorous approaches to this problem, a number of researchers have postulated property-performance relationships for scratch and mar resistance. Unfortunately, these postulated relationships have been rather broad and general within a particular class of polymers, for example, semicrystalline thermoplastic polymers [36] or glassy crosslinked amorphous coatings [55]. Often, these relationships are little more than statements of well-established material mechanics relationships. For example, for crosslinked polymer coatings, scratches with brittle fracture characteristics are typically observed for materials with low toughness and low failure strain, while scratches exhibiting ductile deformation are generally observed for materials that have higher values of toughness and failure strain [55]. For semicrystalline thermoplastics, plastic deformation during scratching has been related to yield stress, elastic modulus, and friction coefficient, while fracture behavior has been related to fracture toughness, elastic modulus, and friction coefficient. The incorporation of specific aspects of scratch testing as related to polymer behavior, for example, rate dependencies, into these relationships has not been done. Most likely, this deficiency is a result of the limited amount of data available with complete descriptions of testing conditions upon which to base such relationships, and the wide range of testing systems and variables used.

The insufficiency of property-performance relationships is most prevalent in the scratch and mar resistance literature for polymeric coatings. Researchers typically acknowledge observing elastic, plastic and fracture processes during scratch testing [17, 46, 49, 55]. Soft, flexible coatings, such as elastomeric coatings, are generally thought to have good scratch resistance properties due to their ability to recover all but the most severe scratch deformations, but these materials often perform poorly in other important aspects [5, 7, 55]. For glassy coatings, good scratch resistance has been associated with low to moderate modulus [6, 13, 14, 55], high toughness [3, 6, 8], high creep rate or degree of recovery [6, 44, 45, 48], high crosslink density [3, 5, 7, 13, 14], and high work of indentation [6]. Other properties and characteristics such as hardness, T_g, tensile elongation at break, and tensile breaking energy have had mixed associations with scratch resistance. Note, however, that in many of these studies, the measure of scratch resistance varied as did the testing conditions. Perhaps the most notable, albeit not particularly helpful, conclusion is that a balance must be found between properties such as toughness, modulus, and yield stress to optimize scratch and mar resistance [13, 14, 55]. This approach of balancing properties is based on minimizing the number and size of scratches caused by the wide distribution of forces and particle sizes that are expected in service condition. However, it essentially ignores viscoelastic behavior, which will be important given the expected distributions of time, temperature, and rate associated with scratches in service conditions.

While less literature is available regarding the scratch and mar resistance of semi-crystalline polymers, the studies tend to be more complete. For example, Xiang et al. [36] have studied a large number of different thermoplastic materials using both the Ford test apparatus and a single-probe progressive scratching device, utilizing the model of Hamilton and Goodman discussed previously to understand the relationships between properties and scratch behavior. In this study, higher values of elastic modulus resulted in smaller penetration depths but increased the stresses local to the contact, which increased the potential for cracking and larger-scale plastic deformation. Thus, with the addition of stiff fillers or an increase in crystallinity, the increased modulus increases the stresses, and the inhomogeneities can cause cracking. With the addition of rubber fillers, modulus decreases but scratch depth increases, potentially causing rubber particle cavitation and debonding. Also, higher values of yield stress result in less plastic deformation but can increase the potential for cracking, and as the coefficient of friction increases, the tendency for brittle fracture or larger plastic damage also increases, because the maximum surface tensile stress increases and the plastic zone shifts toward the surface. Thus, the combined use of modeling and experimentation was useful in understanding some of the relevant property-performance relationships.

Relating Scratch and Mar Resistance to Appearance Attributes

Relating appearance attributes to scratch and mar testing is dependent on the type of test. Specialized appearance metrics, such as gloss or distinctness of image, are based on specular and spectrophotometric properties averaged over a certain area of the sample that is small relative to the overall sample but potentially large with respect to a single scratch. For measurable changes in these appearance metrics, a large number of scratches must be created, which is not often feasible or is time consuming using single-probe testing. Thus, these appearance measurements are most often associated with field and field simulation testing. However, in attempts to reproduce in short tests the damage that occurs in the field over long periods of time, field simulation tests can be much more harsh than actual field conditions. In any case, while appearance metrics can be useful for certain qualitative monitoring of some materials, they are generally inadequate for characterizing surface texture and defect structures such as scratches and mars. Thus, their use in evaluating scratch and mar resistance is limited.

For single-probe scratch testing, appearance is typically alluded to by the term "scratch visibility," which is usually related to the damage mechanisms and associated scratch morphology. The occurrence of brittle fracture during scratching is often associated with increased visibility of scratches compared to scratches for which viscoelastic and/or plastic damage has occurred [13, 14, 17, 20, 28, 36]. Such observations are due mainly to differences in the associated topography (e.g., rougher scratch morphology, cracking, chipping, etc.) and to stress whitening, which is a result of local variations in the magnitude and isotropy of refractive index [30, 36]. However, the overall dimensions of scratches [55] and the material microstructure [44] are also important, regardless of the damage mechanism. Other perception issues can also affect the visibility of a single scratch, such as the color of the sample [55], the relative orientations of incident light, scratch direction, and observer [17], and the time an observer is allowed to view the sample [41]. Accounting for the last of these factors is difficult, but understanding the interaction of light with different polymer surface morphologies and characteristics is possible using appropriate appearance metrology [58].

To date, the use of optical methods to investigate appearance-related issues in single-probe scratch testing is limited. In one study [28], laser profilometry was used to determine the topographic characteristics of scratches created in PMMA under a variety of testing conditions. In addition, the percentage of light reflected from point to point across a scratch was also captured. For these measurements, a narrow wavelength laser was used with incident and detection directions both normal to the surface, and the detector solid angle was approximately 24°. Also, the scratched PMMA was coated with gold so that the measurements were based only on surface features and not on the optical properties of the material. However, the interaction of light with a solid surface, and thus appearance, is a function of wavelength, angle of incidence, angle of observation (detection), as well as the surface geometry and optical properties of the material. Thus, the relationship of the percentage light reflected measured in this fashion to actual appearance characteristics is not clear. Also, because of the limited spot diameter of the laser probe ($\cong$ 1 μm), the scratches were very large (depths of $\approx$ 16 μm and widths greater than 50 μm), and thus the use of this method for scratches and mars created under less severe conditions appears to be limited. The results of the study did indicate that the amount of light reflected from the scratch was higher (i.e., changed less) when ductile deformation was associated with the scratch compared to brittle deformation. Also, the amount of reflected light decreased with increasing load prior to the onset of brittle deformation, perhaps indicating more subtle changes in scratch morphology under conditions of ductile deformation than can be characterized, for instance, in a scratch map.

In another study [30], optical microscopy with reflected polarized light was used with digital image analysis to study and quantify light scattered due to surface deformation of polypropylene (PP) and talc-filled PP. Linearly polarized light was reflected off of the sample surface, and the scattered light was collected after passing through a crossed polarized analyzer. 100X magnification was used, and a video camera image was collected and digitized. The digitizing system was calibrated with a light meter. Measurements of isotropic scattering and anisotropic scattering were calculated from the average and difference, respectively, of reflected intensity with the scratch direction parallel to and at 45° to the incident direction. The measure of isotropic scattering was used as a measure of refractive index changes due to void formation, and the measure of anisotropy was used as a measure of refractive index changes due to molecular orientation. Both of these measures increased for scratches made on PP samples with increasing talc content. Again, however, the actual relationship between these measurements and appearance attributes was not established.

Recommendations

If a standard test method or a set of standard methods are to be developed, statistical aspects of scratch and mar resistance must be addressed. The deformation mechanisms, which will likely be important in determining scratch and mar resistance, develop such that energy dissipation will be minimized. Thus, the relative energies of potential dissipation processes in the contact area will dictate how the deformation develops [20]. These dissipation processes will be related to the local polymer structure, particularly the defect structure, which is likely to vary from point to point over the sample surface as well as from sample to sample. Also, as discussed previously, a polymeric material will encounter distributions of forces, rates, temperatures, particle sizes, and other variables in service. Addressing these many statistical factors presents a significant barrier to the development of standard test methods for scratch and mar resistance.

The two most significant areas that can help to overcome the barriers involved are (1) the development of models and (2) the development of measurements that assess the effects of scratch and mar damage on appearance. Model development must include time-dependent polymer behavior, which has been shown to be extremely important in scratch and mar resistance measurements. Material properties input into the model could include those measured by bulk methods, such as the essential work method [59], but perhaps properties or apparent properties measured using indentation (i.e., measured locally under similar stress states to scratch testing) would be more appropriate. The model would be useful for studying the effects of various test variables such that better test methods could be designed. Further, the relative effects of different material properties could be studied and verified through scratch testing with systematic variation of test variables, all of which would significantly enhance the current level of understanding of property-performance relationships. Critical to such understanding, however, will be determining the effects of scratch and mar damage on appearance, as such effects are at the core of the term "scratch and mar resistance."

Summary and Conclusions

A review of literature related to measuring the scratch and mar resistance of polymeric materials has been presented. Test methods that have been used in various studies include field simulation tests and single-probe tests. While both types of tests have been criticized as being too severe relative to service conditions, field simulation tests further lack the necessary control over test variables and a quantitative basis for making relevant measurements. Single-probe tests offer a more fruitful alternative for determining property-performance relationships, because measurements and control over test variables are significantly more robust. An exception is the use of atomic force microscopes, which to date lack the robust control and measurement capabilities exhibited by depth-sensing indentation systems for performing scratch tests. Because of the wide variability between various scratch tests and the sensitivity of polymers to the scratch test conditions, comparisons of different studies has been difficult, in part leading to a lack of understanding of important property-performance relationships related to scratch and mar resistance.

Qualitative assessment of scratch behavior in the form of scratch maps has helped to show the wide range of deformation modes exhibited by polymers relative to metals and ceramics within a relatively narrow range of contact variables. However, quantitative measurements that incorporate the appearance component of the problem and the development of models that include time-dependent behavior are lacking. Further progress in both of these areas is required to better understand scratch and mar resistance. Until then, scratch testing will continue to provide inadequate information for predicting the performance of a polymeric material in service conditions.

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