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Rubber particle size and type effects on scratch behavior of styrenic-based copolymers

Mohammad Motaher Hossain [a], Ehsan Moghbelli [a], Eike Jahnke [b], Philipp Boeckmann [c], Svetlana Guriyanova [c], Ralf Sander [c], Rolf Minkwitz [c], Hung-Jue Sue [a], *

[a] Polymer Technology Center, Department of Materials Science and Engineering, Texas A&M University, College Station, TX, 77843, USA
[b] Styrolution Group GmbH, 60325, Frankfurt, Germany
[c] BASF SE, Advanced Materials & Systems Research, 67056, Ludwigshafen, Germany

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ABSTRACT

Effects of rubber particle size and type on scratch performance were investigated using two types of styrenic copolymers: acrylonitrile styrene acrylate (ASA) and acrylonitrile butadiene styrene (ABS). ASAs with rubber particle sizes of 100 nm and 1 μm, respectively, and ABS with rubber particle size of 100 nm were examined. Linearly increasing normal load scratch tests were performed according to the ASTM D7027/ISO 19252 standard. A noticeable drop in scratch resistance is found in ASA with 100 nm rubber particles when compared to ASA containing 1 μm rubber particles. ABS is observed to exhibit a higher scratch resistance when compared to ASA with comparable rubber particle size. Detailed deformation and damage mechanisms have been investigated to explain the observed differences in scratch performance of the model systems. Implication of the present findings for design of scratch resistant polymers is discussed.

1. Introduction

Although there has been wide usage of polymeric materials in engineering, coating and packaging applications, polymer scratch behavior is still a topic of significant research interest in industry and academia due to their low resistance to surface deformation and damage. Scratch, which entails a rigid tip simultaneously indenting and traversing a material surface, is considered as a single pass and single asperity category of test in tribology [1,2]. Various experimental techniques have been developed over the years to measure the scratch resistance of polymers with limited success [3–7]. Recently, a standardized test methodology, designated as the ASTM D7027/ISO 19252 standard [8,9], has been established and used extensively for quantitative evaluation of polymer scratch resistance. The application of an increasing normal load, as prescribed in the standard, generates progressive surface deformation with distinctive damage transitions throughout the scratch path which may include onsets of groove formation, fish-scale development, micro-cracking, and plowing. Identification and analysis of these damage transitions are important for fundamental understanding of polymer scratch behavior. By employing the ASTM standard, numerous quantitative scratch performance evaluation and structure-property relationship investigations have been carried out [8,10–14]. Finite element analysis has also been employed for in-depth understanding of scratch-induced deformation mechanisms to establish material and surface properties-scratch behavior relationship [13,15–23].

Several attempts have been made to categorize the observed scratch damage features into scratch-deformation maps that correlate the formation of different scratch damages with material properties and testing condition [13,24–26]. By using a three-dimensional finite element method (FEM) analysis, Jiang et al. [13] showed that the material beneath the scratch tip experiences a compressive stress state while the material near the surface behind the scratch tip experiences a high magnitude of tensile stress. Based on this understanding, Hossain et al. [15–17] showed that yield stress, strain at stress recovery and strain hardening slope in compression are the most important parameters that influence the scratch groove formation. Tensile behavior has little influence on groove formation but does correlate with surface cracking, crazing, and debonding along the scratch path, which lead to surface roughening and greatly increase scratch visibility [16]. Using

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* Corresponding author. Tel.: +1 (979) 845 5024; fax: +1 (979) 845 3081.
E-mail address: hjsue@tamu.edu (H.-J. Sue).

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styrene-acrylonitrile (SAN) random copolymers with similar compressive behavior, Browning et al. [1] showed that an increase in tensile strength delays the onset of microcrack formation. Since the material and surface properties can be related with the scratch-induced deformation, quantitative prediction of polymer scratch behavior using FEM was performed [18]. The result shows that indeed by knowing the material behavior and surface properties, scratch behavior of polymers can be predicted [18]. The scratch studies mentioned above were largely based on homogeneous single-phase polymers.

Although numerous studies on polymer scratch behavior have been carried out, significant research efforts are still needed to better understand the scratch-induced deformation and damages in polymers, specially, in multi-phase polymeric systems. For instance, in-depth analysis on the roles rubber particles play on scratch performance of rubber-modified polymers is still lacking. Even though rubber particles can act as impact modifiers to increase toughness and ductility, they can also reduce modulus and strength of the polymeric system [27,28], which complicates their influence on scratch behavior. Furthermore, choice of processing condition can significantly affect their final phase morphology and skin-core characteristics.

In a recent study on a soft thermoplastic olefins (TPOs) that consists of 70 wt.% ethylene-propylene rubber (EPR) and 30 wt.% polypropylene (PP), Browning et al. [11] observed that the crystallinity of the ethylene segment and the internal morphology of the EPR phase significantly affect the scratch behavior of the soft TPOs. In another study, Moghbelli et al. [12] showed that the degree of surface crystallinity can significantly influence the scratch behavior of PP. The findings suggest that: i) the surface or subsurface phase morphology of semi-crystalline polymers, which can be modified by altering the processing condition, plays an important role in polymer scratch behavior, and ii) the material properties near the surface of a semi-crystalline polymer, which significantly affect the scratch performance, are likely to be different from those of the bulk. Moghbelli et al. [14] further showed that improvements in tensile strength and modulus by adding synthetic clay nanoplatelets or fracture toughness and ductility by inserting core-shell rubber (CSR) nanoparticles do not enhance the scratch performance in epoxy. In a more recent study [2], it has been shown that the scratch performance of rubber-modified acrylonitrile styrene acrylate (ASA) system generally deteriorates with increasing rubber content due to the reduction in tensile and compressive yield strengths.

The present research focuses on investigating how the rubber type and size influences scratch behavior of styrenic-based copolymers. Both acrylonitrile styrene acrylate (ASA) and acrylonitrile butadiene styrene (ABS) are composed of styrene-acrylonitrile (SAN) matrix and a rubber phase. The core of ABS is butadiene rubber, while that of ASA is an acrylic rubber. Extensive analysis has been performed to understand the observed differences in scratch behavior and evolution of different scratch-induced surface deformation mechanisms. Implication of the present study for designing scratch resistant rubber-modified polymers is discussed.

2. Experimental

2.1. Materials

The ASA and ABS copolymers utilized in this study were provided by Styrolution Group GmbH (Frankfurt, Germany). The ASA systems consist of a random copolymer SAN matrix and grafted polybutyl-acrylate (PBA) rubber particles with an average nominal diameter of 100 nm and 1 μm, respectively. In the SAN phase, the acrylonitrile content was controlled to be at 35 wt.%, and the weight-average molecular weight (Mw) of SAN was chosen to be 104 kg/mol [2]. The ABS system consist of a random copolymer SAN matrix and grafted polybutadiene (PBD) rubber particles with an average nominal diameter of approximately 100 nm. Within the SAN phase the same material as described for ASA was used. The rubber concentration was 30 wt.% for all the systems investigated.

Test specimens were fabricated by injection molding with a fan gate design to spread and slow the melt as it enters the mold cavity to ensure near-uniform molecular orientation across the width of the plaques. The plaques were 150 mm × 150 mm in rectangular shape and 6 mm in thickness. Upon receipt, all the plaques were dried in a vacuum oven overnight at 80 °C with a vacuum pressure of 30 mm Hg. Nomenclature and RMS roughness values, measured on an area of 525 μm × 700 μm, of each system, are listed in Table 1. According to the roughness measurement, surface finish of all the model systems was smooth with no appreciable difference among them.

2.2. Scratch tests

Scratch tests were carried out according to the ASTM D7027-05 standard [9] by using a progressive normal load range of 1–70 N at constant scratch speed of 100 mm/s for a length of 100 mm. A stainless steel scratch tip with spherical geometry was used. The diameter of the scratch tip was 1 mm. A minimum of five scratch tests were performed at room temperature on each plaque in the direction same as the melt flow direction of the sample.

2.3. Post-scratch analysis

Scratch damage analysis was carried out 24 h after the completion of scratch tests to allow for viscoelastic recovery. The critical normal loads for the onsets of groove formation, cracking, and plowing were measured using a Keyence VK9700 Violet Laser Scanning Confocal Microscope (VLSCM). The onset points for micro-cracking and plowing were directly observed under the microscope. The onset of groove formation was determined using the height profile obtained from topographical imaging *via* VLSCM.

2.4. Mechanical property characterization

Dog-bone shaped specimens for tensile testing based on ASTM D638 [29] type I geometry were prepared by BASF SE (Ludwigshafen, Germany). The nominal length, thickness, and width of the narrow section were 170, 4, and 10 mm, respectively. The test was performed at constant crosshead speed of 5 mm/min under ambient temperature using a screw-driven Sintech2 load frame equipped with a 30 kN load cell and MTS632 extensometer. High strain rate tensile testing was also performed at constant crosshead speed of 250 mm/min using a screw-driven MTS Insight load frame equipped with a 30 kN capacity load cell.

Specimens for uniaxial compression testing were prepared using plaques with 6 mm thickness. The compression specimens were precisely cut by an Isomet 1000 Precision Saw into prisms with sharp, clean edges. The surfaces of the specimens were carefully polished using 4000 grit silicon carbide polishing paper. The

Table 1
Material information and surface condition of model systems.

	Rubber type	Structure type	Rubber particle size	RMS roughness, μm
ASA100	ASA	SAN grafted PBA rubber	≈100 nm	0.08 ± 0.01
ABS100	ABS	SAN grafted PBD rubber	≈100 nm	0.05 ± 0.00
ASA1000	ASA	SAN grafted PBA rubber	≈1000 nm	0.07 ± 0.00