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Effect of thermal history on scratch behavior of multi-phase styrenic-based copolymers

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ABSTRACT

Effect of thermal history on scratch performance of acrylonitrile styrene acrylate (ASA) and acrylonitrile butadiene styrene (ABS) model systems was studied. ASAs with rubber particle sizes of 100 nm and 1 μm, respectively, and ABS with rubber particle size of 100 nm were investigated. Linearly increasing normal load scratch tests were performed according to the ASTM-D7027/ISO-19252 standard. An improvement in scratch resistance is observed in ASAs when annealed at 140 °C whereas a noticeable drop in scratch resistance is found in ABS under the same condition. Various microscopic analyses were conducted to determine the corresponding deformation mechanisms for the observed dependence of scratch performance on annealing. Implication of the present findings for design of scratch resistant rubber toughened polymers is discussed.

1. Introduction

Scratch behavior of multi-phase polymeric systems is gaining significant interests due to its increasingly wide usage in engineering, and structural and durable goods applications. However, in-depth understanding of scratch-induced surface deformation in multi-phase polymeric systems is quite challenging since the presence of micro- and nano-phase domains near the surface can greatly influence the scratch deformation and damage [1]. It is not straightforward to relate the surface deformation and damage phenomena to bulk mechanical properties in multi-phase polymeric systems. For instance, rubber addition to the matrix improves toughness and ductility but simultaneously reduces modulus and strength [2,3], which complicates the fundamental understanding of their influences on scratch behavior.

For homogeneous single-phase polymers, researchers have shown some success in correlating material and surface properties to the evolution of different scratch-induced surface damage features [4–24]. Using the ASTM D7027/ISO 19252 scratch test standard [25], it has been shown that an increase in tensile strength delays the onset of microcrack formation during scratching in styrene-acrylonitrile (SAN) random copolymers [5]. Bucaille et al. [7] showed that a more pronounced strain hardening can improve scratch resistance, defined as the resistance to surface deformation and damage due to sliding indentation of a rigid asperity, since it restricts large-scale plastic deformation. Using the finite element method (FEM) parametric study and experimental observation, it has been shown that, in addition to the coefficient of friction, yield stress, strain at stress recovery and strain hardening slope in compression are the most important material parameters that determine the development of scratch groove during scratching [9–11]. Tensile behavior has little influence on scratch groove formation but correlates well with microcrack formation during scratching [9–11]. In a recent study [26,27], it has been shown that by knowing the material behavior and surface characteristics, the scratch behavior of polymers can be quantitatively predicted with reasonable accuracy.

For multi-phase polymeric systems, understanding and analysis of the scratch behavior is rather complex. In-depth understanding of the localized deformation and damage due to interaction between the micro-/nano-sized particles and matrix is needed. Introduction of a rubber phase in a polymer matrix has shown to significantly alter the stress state near the rubber particles [28–31], which could ultimately change the deformation mechanisms. Browning et al. [32] showed that the crystallinity of the ethylene segment and the internal morphology of the ethylene-propylene rubber (EPR) phase significantly affect the

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scratch behavior of soft thermoplastic olefins (TPOs). In another study [33], it has been shown that the degree of surface crystallinity, which can be modified by varying the processing conditions, can significantly influence the scratch behavior of polypropylene (PP). It was further shown that [34] improvements in different bulk mechanical properties by adding synthetic clay nanoplatelets or core-shell rubber (CSR) nanoparticles in epoxy do not necessarily enhance the scratch resistance. Liang et al. [35] showed that the scratch resistance of rubber-modified acrylonitrile styrene acrylate (ASA) system deteriorates with increasing rubber content due to reduction in tensile and compressive properties. In a more recent study [1], Hossain et al. reported a reduction in scratch resistance in ASA containing 100 nm rubber particles when compared to ASA containing 1 μm rubber particles. It was further shown that rubber type has significant influence on scratch behavior as acrylonitrile butadiene styrene (ABS) exhibits a higher scratch resistance when compared to ASA with comparable rubber particle size. Since the bulk mechanical behaviors in tension and compression of the model systems are similar, they were not so useful in explaining the observed difference in scratch resistance in the rubber-modified systems. It was argued [1] that the rubber particle type and size can alter the damping characteristics of the SAN matrix, hence the frictional behavior to cause variation in their scratch behavior.

Thermal history has long been shown to significantly affect the physical and mechanical properties of different polymers. Variation in processing condition can induce and alter skin-core characteristics and significantly affect the final morphology, especially on sample surfaces. However, for styrenic-based copolymers, it has been shown that the processing conditions have insignificant effect on mechanical properties [36,37]. In particular, tensile yield stress and Charpy impact strength have been shown to remain the same upon variation in heat treatment procedure. It was also shown that [37] high temperature annealing can improve the scratch resistance without influencing the bulk properties in rubber-modified styrene-acrylonitrile (SAN) systems.

The present study focuses on understanding how the thermal history influences the scratch behavior of styrenic-based copolymers. The model systems, acrylonitrile styrene acrylate (ASA) and acrylonitrile butadiene styrene (ABS) are composed of SAN matrix, and acrylic and butadiene rubbers, respectively. Extensive analysis has been performed to understand the observed differences in scratch resistance and evolution of different scratch-induced surface deformation mechanisms. Implications of the present study for designing scratch resistant rubber-modified polymers are discussed.

Table 1
Material information of model systems.

	Rubber type	Structure type	Rubber particle size
ASA100	ASA	SAN grafted PBA rubber	≈ 100 nm
ABS100	ABS	SAN grafted PBD rubber	≈ 100 nm
ASA1000	ASA	SAN grafted PBA rubber	≈ 1 μm

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. Size distribution of the rubber particles in the model systems can be found elsewhere [1]. 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 [1] with a polydispersity (PDI) of 3.7. The ABS system consisted 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 is 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. Nomenclature and physical characteristics of each system are listed in Table 1.

2.2. Heat treatment

Upon receipt, all the plaques were dried in a vacuum oven for 12 h at 80 °C with a vacuum pressure of 30 mm Hg. The drying process was conducted by sandwiching the plaques in between two smooth glass plates (Surface roughness, $R_a = 17.0$ nm, $R_q = 22.3$ nm). An external weight leading to stress of about 10 kPa was applied to the sandwiched samples during heating and cooling to prevent the potential for uneven residual stress relief or warping of the plaques. After drying, the high temperature annealing (HTA) process was carried out on one of the two dry reference plaques for each system studied. The HTA process was conducted at 140 °C, which is about

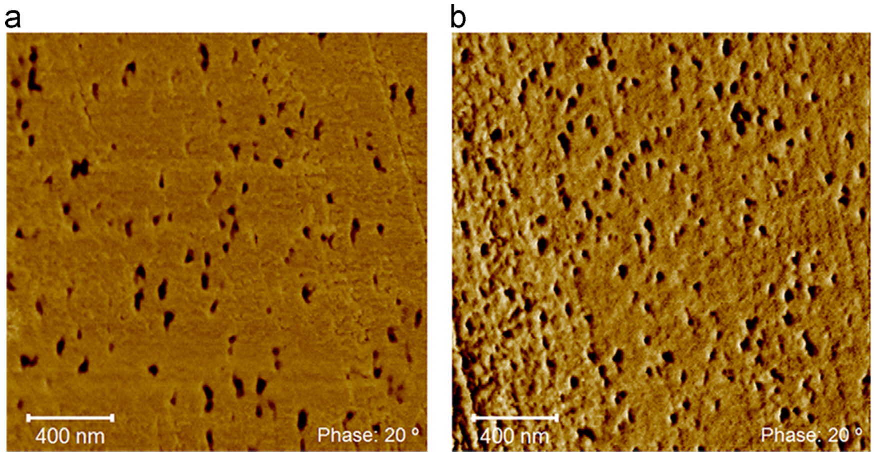

Fig. 1. AFM micrographs of the ASA100 cross-section in the sub-surface, (a) dry reference sample and (b) HTA sample.