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Study of the scratch resistance criteria and their relationship with mechanical properties and microstructure in a ternary thermoplastic blend

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ABSTRACT

Polymeric materials generally suffer from a low resistance to various types of surface mechanical damage, among which scratch is a prominent example. While several attempts have been made to assess the scratch resistance and its relationship with the bulk mechanical properties in simple polymeric systems, the available research on the polymeric blends is scarce. This study attempts to fill this gap by studying the link between the scratch resistance and mechanical properties in a ternary polymeric nanocomposite, which has proved to feature superior and tunable mechanical properties. For this aim, blends of polypropylene and polyamide 6 were prepared using melt blending with two different types and various amounts of compatibilizers. Their microstructure was studied using scanning electron microscopy and atomic force microscopy. It was observed that the type of morphology depends upon both compatibilizer type and content. Bulk mechanical properties were investigated at different loading conditions. The microstructure was seen to have a noticeable effect on ductility of the blends. Different scratch groove geometry parameters were seen to be affected by different mechanical properties. It was shown that relying exclusively on scratch groove geometry might lead to contradicting conclusions regarding the effect of bulk mechanical properties on scratch resistance. Instead, a heavier emphasis was placed upon the respective contribution of each parameter to the overall scratch visibility. In addition, it was shown that micromechanical scratch deformation mechanisms have a crucial impact on scratch visibility, and they are affected by a complex interplay among various mechanical properties. An analysis of these relationships is provided with the aim of moving towards a comprehensive understanding of scratch visibility and routes to its minimization.

1. Introduction

Polymeric materials are used in numerous everyday items. While their substitution for traditional materials like metals and wood has made it possible for the manufacturing industry to produce goods at higher rates and lower cost, it has certain drawbacks. For example, the surface of polymeric materials is generally very susceptible to mechanical damage. A scratch on the surface of a polymeric material is a large size flaw that can potentially be a stress raiser restricting the applicability of the part during certain service conditions. Equally important is the fact that the surface damage caused by scratching detracts from the subjective perception of quality and limits the application of the material. Therefore, it is crucially important to gain insight into the principles of scratch resistance in polymers.

Several attempts aimed at understanding the micromechanical mechanisms of scratch have been reported [1–13]. Briscoe et al. [1,2] conducted some of the first comprehensive studies on the scratch deformation modes in polymers. They identified various mechanisms such as fully elastic, ironing, ductile ploughing, and machining, and developed maps that attempted to predict which of these mechanisms would be dominant at various test conditions. The presented maps vary vastly for different polymers [1,13]. Briscoe and Sinha [6] later published a review that summarized the findings regarding the effects of scratch test configurations on the deformation behavior of polymers.

Xiang et al. [3] carried out some numerical stress analysis for the case of spherical indenters, and compared the scratch depth for a number of polymeric materials. They concluded that increasing the rigidity of polymers might enhance or deteriorate scratch resistance in different cases. In general, scratch visibility was concluded to be the result of a complex interplay among tensile parameters, friction coefficient, and viscoelasticity. Jiang et al. [10] studied the effect of increasing normal load on the scratch deformation mechanisms of four polymers with different tensile behaviors, and the reported results reveal how the response of each polymer is clearly different from the rest.

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Kurkcu et al. [14] studied the effect of rigid and rubbery fillers on two different polymers. They observed a relationship between scratch hardness and yield strength in pure polymers. But their results showed no such relationship in the case of blends and composites. More interestingly, they showed that adding rigid fillers, while increasing scratch hardness, deteriorates scratch visibility.

Lubricating agent was found to be an effective way for improving scratch visibility, confirming the critical role of friction coefficient in determining the nature of microscopic surface damage [15,16]. The effect of test conditions such as indenter velocity and normal load has also been investigated for various polymers, and various results regarding the effect of these parameters on scratch micro-mechanisms have been reported [4,9,17–21]. After careful review of the above-mentioned and similar studies, one can come to the conclusion that a great amount of research is still needed, before a comprehensive guideline can be developed that predicts scratch behavior of a material not previously tested. In the meantime, material-specific studies are required to assess the scratch performance of various polymeric systems. Among different polymers studied for their scratch resistance, polypropylene (PP) stands out, due to its versatility and extensive breadth of applications, in which visual appearance of the parts has a priority.

Most of the research on the scratch resistance of polypropylene has focused on the effect of mineral fillers [9,15,16,22–27]. It has been reported that adding micrometric talc and wollastonite leads to deterioration of scratch depth and visibility, mostly due to particle debonding [15,16]. Dasari et al. [22] showed that using high crystallinity polypropylene leads to a better scratch performance. In addition, ethylene-propylene diblock copolymers were shown to feature a lower scratch resistance, compared to both long-chain and short-chain polypropylene. Two separate publications reported that wollastonite-filled and talc-filled polypropylene have a lower scratch resistance than neat PP, in spite of their higher elastic modulus [23,26]. Incorporation of a coupling agent was shown to reverse this trend, owing to the improved particle-matrix bonding.

Zokaei et al. [9] conducted a comprehensive study on the effect of nanometric calcium carbonate on the scratch behavior of homo- and co-polypropylene. They took the inverse of scratch contour length as the representative of scratch resistance. Considering this criterion, they reported that the mentioned nano-sized fillers increase the scratch resistance of homo-PP, but not co-PP. They observed a general relationship between scratch resistance and both elastic modulus and fracture toughness in the system under study. Another study reported considerable improvement in scratch resistance of polypropylene by adding graphene oxide and compatibilizer [24].

Jiang et al. [28] focused their research on the so-called *stick-slip* phenomenon in neat polypropylene, and the resulting *fish scale* morphology. They presented the conjecture that the distance between the successive fish scale markings can represent the scratch resistance in PP-based materials. Qin et al. [19] reported that mineral fillers were ineffective in controlling scratch damage in polypropylene. However, adding lubricants and increasing crystallinity were observed to deter more brittle scratch mechanisms, to some extent. Another study evaluated the effect of deformation rate on the scratch behavior of polypropylene, and concluded that higher scratch rates lead to lower critical load required for the onset of scratch visibility [18]. Effect of mold temperature on the scratch performance was studied by Kobayashi et al. [29] who found that increasing mold temperature will improve scratch resistance through enhancing crystallinity [29]. The same study found the type of PP crystals to be irrelevant in determining scratch resistance. Similar results had been reported earlier [30].

To the best of our knowledge, the extent of research conducted on polypropylene thermoplastic blends is very limited [31], and no research has been published on the analysis of the scratch performance in polypropylene/polyamide blends and its correlation with compatibilizer type and content. In addition to addressing this subject, this study aims to assess and compare various scratch resistance criteria. Moreover, the wide range of ductility observed among the samples allowed for the investigation of the mechanisms through which bulk mechanical properties affect scratch resistance parameters. Special attention is paid to the subject of scratch visibility, and the effect of incorporation of a rubbery compatibilizer on the micromechanical processes that affect this parameter.

2. Experimental

2.1. Materials

An injection grade polypropylene (PP) with the trade name 500 M from Navid-Zarshimi Petrochemical Co. and a polyamide 6 (PA6) with the trade name Akulon F223 from DSM were used as the polymer matrices. Two different compatibilizers were incorporated in this study. Polypropylene grafted with maleic anhydride (PP-g-MA), was obtained from Dupont under trade name Fusabond MU613U05. The second compatibilizer was Kraton FG1901X, a linear triblock copolymer based on styrene and ethylene/butylene with a polystyrene content of 30 wt% and grafted with maleic anhydride (SEBS-g-MA). The latter acts as both compatibilizer and rubber modifier.

2.2. Sample preparation

All the samples contained 70 wt% polypropylene, and the remaining was a sum of various amounts of PA6 and either PP-g-MA or SEBS-g-MA. The sample codes and their contents are listed in Table 1. All the samples contained 0.5 wt% black PP masterbatch, which provided a consistent black color for all the specimens. The intent was to eliminate the effect of varying color and gloss on the scratch visibility. Before dry-blending, all the materials were vacuum-dried for 24 h at 80 °C. Melt compounding was carried out in a Nanjing Giant twin-screw extruder (L = 1.2 m, D = 53 mm). The temperature varied from 190 °C in the feeder to 245 °C in the nozzle. The screw speed was set to 300 rpm. The materials were then injection molded in the form of standard tensile and Charpy impact specimens. The same temperature range was used for injection molding. The conditions were identical for all the samples.

2.3. Microstructure analysis

Scanning electron microscopy (SEM) was utilized to investigate both morphology and scratch deformation mechanisms. The former was studied on cryo-fractured Charpy specimens, with the fracture direction perpendicular to the flow direction. Some samples were etched in formic acid or toluene to selectively remove PA6 and SEBS-g-MA, respectively. These samples were etched for two hours at 50 °C. All samples were gold coated prior to SEM imaging. Two different SEM machines were used: A Philips XL30 and a Tescan Vega. The instruments were operated at 25 kV and 15 kV, respectively. Atomic force

Table 1
The list of sample codes and the respective ingredients.

Sample code	Contents (wt%)			
	PP	PA6	PP-g-MA	SEBS-g-MA
PP	100	0	0	0
S0 (P0)	70	30	0	0
P5	70	25	5	0
P10	70	20	10	0
P15	70	15	15	0
P20	70	10	20	0
S5	70	25	0	5
S10	70	20	0	10
S15	70	15	0	15
S20	70	10	0	20