Organoclay Imparts Scratch Resistance

Modified Clay-Based Additives Improve the Surface Properties of Polyamides, Acrylates and Polycarbonate

Scratches and marring limit the potential applications of thermoplastics, which is why many processors are searching for approaches to protecting surfaces from such damage. To address this issue, various thermoplastics have been combined with additives based on modified clay and then had their properties compared.

Thermoplastic surfaces, for instance on domestic appliances, are exposed to scratching and damage in everyday service. Adding organoclay increases the scratch resistance of thermoplastics, thus protecting surfaces (© TenasiTech)

Many thermoplastics are not resistant to scratching and marring, which limits their potential applications (**Title figure**). For the purposes of the present article, "scratches" are damage caused by drawing a hard or sharp object under force over a surface. "Abrasion" is the grinding away of material from a surface, while wear marks affecting color, gloss or haze but involving no significant loss of material are denoted "marring". There is therefore a need for more resilient surfaces which retain their aesthetics over an extended period [1]. Scratch resistance may be achieved either by hard coatings which are applied during [2, 3] or after [4] processing or by using specific additives. However, hard coats, such as solvent-based, UV- or thermally cured acrylates and polysiloxanes, significantly increase manufacturing costs and preclude further processing of the coated product. Limitations do, however, also apply to conventional plastics additives, such as amides [5], silicone oil [6], siloxanes [7] or very fine fillers [8]. An amide, for example, provides very effective, short-term protection during manufacture, but this will quickly decline in service. Silicone oils and grafted polymers can have an impact on paintability and odor if they migrate onto the surfaces of the molded parts.

Chemical Modification Influences Resistance

Organoclay additives provide a cost-effective, environmentally friendly, durable and paintable alternative. These additives are clays which have been modified with an organic modifier to change the surface chemistry of the clay. Normally a clay surface will have metal ions ionically bound to the surface, most commonly sodium or calcium. The amount will vary depending on the clay. To improve interaction with polymers, the metal ions are exchanged for charged long-chain organic com- »

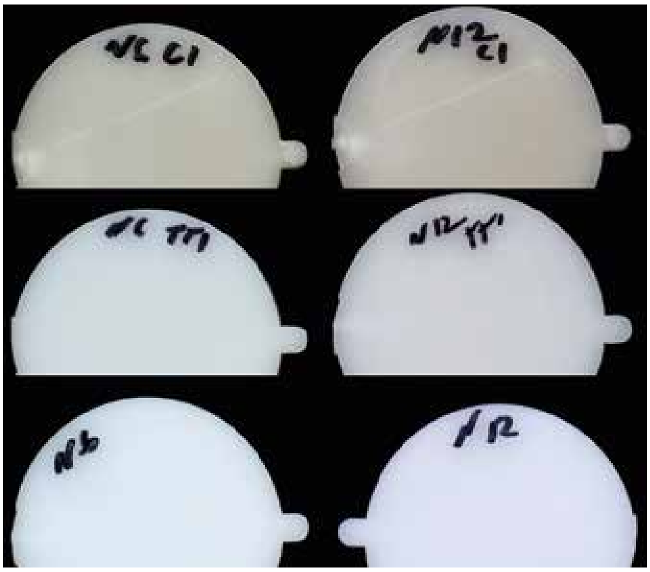

Fig. 1. Color of injection molded polyamide: PA6 (Akulon K222-D, left) and PA12 (Rilson AMNO, right). From top to bottom: with 1% Cloisite 11, with 1% Solid-TT, uncompounded. The resin discolored with Cloisite 11 because the additive suffered thermal degradation (© TenasiTech)

pounds, most often based on amines or pyridiniums. Thermoplastics combined with such additives can be compounded, extruded, injection molded and thermoformed.

Previous studies into these additives have mainly focused on mechanical properties. The literature contains no studies into the effects on scratch and abrasion resistance for polymethyl methacrylate (PMMA), but there are some for polyamide 6 (PA6) and polycarbonate (PC) [9, 10]. The reports for PA6 are inconsistent. For instance, a PA6 nanocomposite made by in-situ polymerization with a 12-aminododecanoic acid-modified montmorillonite clay [11] was found to provide 50 % better Taber test values than the neat polymer. In contrast, [12–14] reported a decrease in scratch resistance for the same PA6 composite when tested with a pin-on-disc tribometer or Taber 5135 abrader. The first test, however, is a mar test, while the latter two methods are scratch tests.

Further, [15] reported a PA6 nanocomposite made by twin screw extrusion using a dioctadecyldimethylammonium ion-modified montmorillonite which exhibited distinctly increased abrasion resistance in a pin-on-disc tribometer test, both compared to the neat polymer and to a nanocomposite based on unmodified montmorillonite. The nature of the chemical modification of the organoclay thus has an influence on scratch and mar resistance. One study of the scratch resistance of PC incorporating 1 wt. % of quaternary ammonium-modified montmorillonite [16] revealed an 88 % reduction in friction coefficient and two orders of magnitude less wear. No further details about the chemical modification of the organoclay were provided and the product is not commercially available.

Interactions between Matrix, Clay and Modifier

The results would suggest that variation can be expected depending on which polymers and organic modifiers are used for the particular organoclay in order to achieve the desired dispersion. The described studies relate to PA6, PA12, PMMA and PC while the two organoclay products are Cloisite 11 (manufacturer: BYK Additives & Instruments), a natural bentonite modified with benzyl, hydrogenated tallow and dimethylammonium chloride, and Solid-TT (manufacturer: TenasiTech Pty Ltd., Marblehead, MA/USA), a synthetic hectorite modified with choline chloride and oleylmethylbis-(2-hydroxylethyl) ammonium chloride. Results for Cloisite

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Measurement Data

Tables and graphs showing the results for gloss measurement, pencil hardness, mar resistance, a wide range of mechanical parameters and test methods, equipment and standards can be found online at
- **www.kunststoffe-international.com/2585177**

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References & Digital Version

- You can find the list of references and a PDF file of the article at *www.kunststoffe-international.com/2585177*

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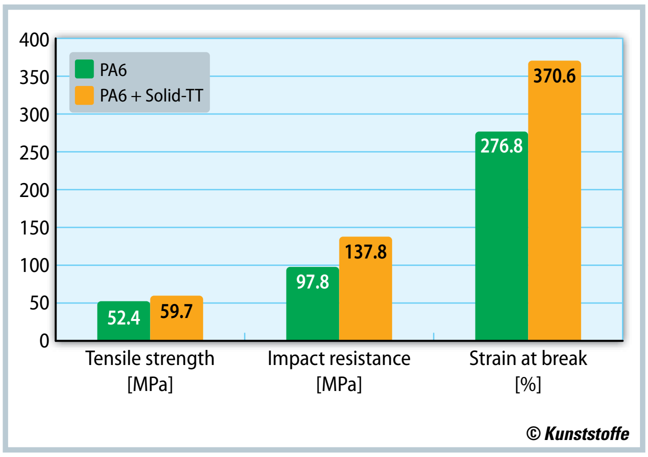

Fig. 2. Testing of the mechanical properties of PA6 (Nycoa 1637) with Solid-TT in comparison with unfilled, processed polymer revealed increased strain at break and impact resistance (source: TenasiTech)

30B and Solid-TT in PMMA are included since Cloisite 30B is an organoclay for engineering plastics which, while now no longer available, has been extensively studied.

Organoclay can be incorporated by in-situ polymerization or melt compounding [17]. Providing there is good compatibility between the polymer and organoclay and the latter has been properly exfoliated (forcing apart of the initial highly aligned stacks through chemical, mechanical and thermodynamic forces), twin screw extrusion provides composites with similar characteristics to those produced by the in-situ method [18]. This simplifies the manufacture of organoclay composites in many different polymers.

Table 1 lists the materials used in this study. Determining scratch, mar and abrasion resistance is complicated by the fillers having an impact on scratch visibility and smooth and grained surfaces differing in sensitivity. Beyond the determination of short-term scratch resistance (e.g. during manufacture), describing long-term behavior in service may require accelerated ageing tests and consideration of weathering and moisture absorption. Moreover, results from the many common methods for measuring scratch resistance are not usually directly comparable [17]. This is why results for different test methods are described below. The additives were in each case incorporated into the melt at 1 wt.% by twin screw extrusion. The reference samples were not compounded. To ensure a more realistic comparison, data are additionally included for a PA6 (Nycoa 1637, manufacturer: Nylon Corporation of America, Manchester, NH/USA) in which both the organoclay composite and a "processed blank" are passed through the same twin screw extruder.

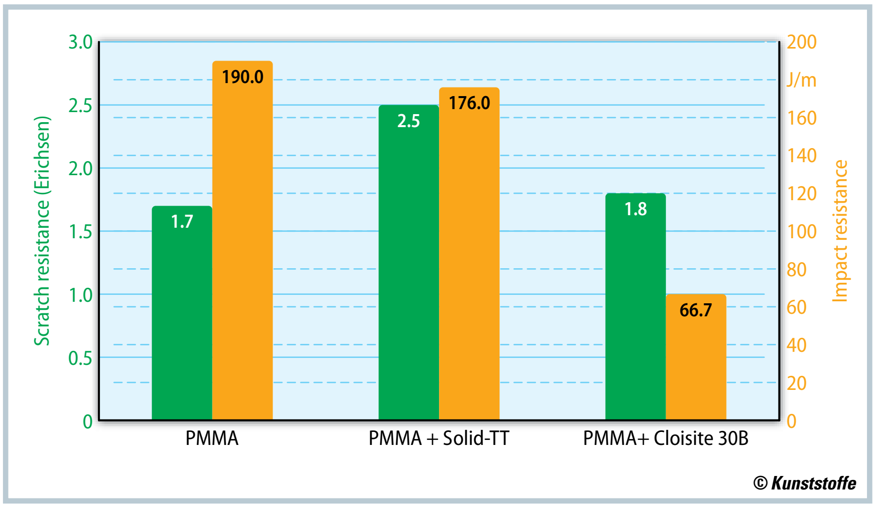

Fig. 3. Radial scratch (Erichsen) (green) and impact resistance (yellow) results for PMMA with Solid-TT or Cloisite 30B (source: TenasiTech)

Material	Trade name and description	Manufacturer
PMMA	Plexiglas V825	Arkema
PA6	Akulon K222-D	DSM Engineering Plastics
PA6	Nycoa 1637	Nycoa
PA12	Grilamid TR90	EMS-Grivory
PA12	Rilsan AMNO	Arkema
PC	Lupoy PC 1201-22	LG Chem
Organically modified organoclay	Cloisite 11: natural bentonite, modified with benzyl, hydrogenated tallow and dimethylammonium chloride	BYK Additives
	Cloisite 30B: natural montmorillonite, modified with methyl, tallow, bis(2-hydroxyethyl) ammonium chloride	
	Solid-TT: synthetic hectorite modified with choline chloride and oleylmethylbis-(2-hydroxylethyl) ammonium chloride	TenasiTech

Table 1. Overview of materials and additives used (source: TenasiTech)

Material	Erichsen scratch test (ISO 4586-2, modified, [N])	Taber abrasion (H18, 1000 g, 1000 cycles) (weight loss, [mg])
PMMA	1.7	-
PMMA + 1% Solid-TT	2.5	-
PMMA + 1% Cloisite 30B	1.8	-
PA6	0.7	5.37
PA6 + 1% Solid-TT	1.2	5.80
PA6 + 1% Cloisite 11	0.95	8.01
PA12 (Rilsan AMNO)	0.9	1.56
PA12 (Rilsan AMNO) + 1% Solid-TT	0.95	1.76
PA12 (Rilsan AMNO) + 1% Cloisite 11	0.75	1.89
PA12 (Grilamid TR90)	2.2	-
PA12 (Grilamid TR90) + 1% Solid-TT	3.4	-

Table 2. Erichsen scratch and Taber abrasion results (source: TenasiTech)

Comparative Results for the Organoclay Additives

Solid-TT increased pencil hardness in all the studied polymers with minimal effect on impact resistance. Discoloration occurred in PC. Cloisite 11 brought about less marked improvements in polyamides. In radial scratch (Erichsen) testing, Solid-TT increased loading force for all studied polymers and did so more than did Cloisite 11. Cloisite 11 reduced scratch resistance in PA12 (**Table 2**). In radial abrasion testing, the results for both organoclay additives were negative, with Cloisite 11 performing worse. Measurement of mar resistance (Crockmaster) revealed increased resistance to scratching with Solid-TT in PA12 (Grilamid TR90).

Solid-TT also provided better results in terms of physical and mechanical properties. Due to the higher thermal stability of Solid-TT, composites produced with it exhibited less color change than when using Cloisite 11 (**Fig. 1**). In Nycoa 1637, Solid-TT increased strain at break by 41 % and impact resistance by 34 % (**Fig. 2**). Grilamid TR90 with the additive exhibited only a slight loss in gloss in comparison previously unprocessed material. The »

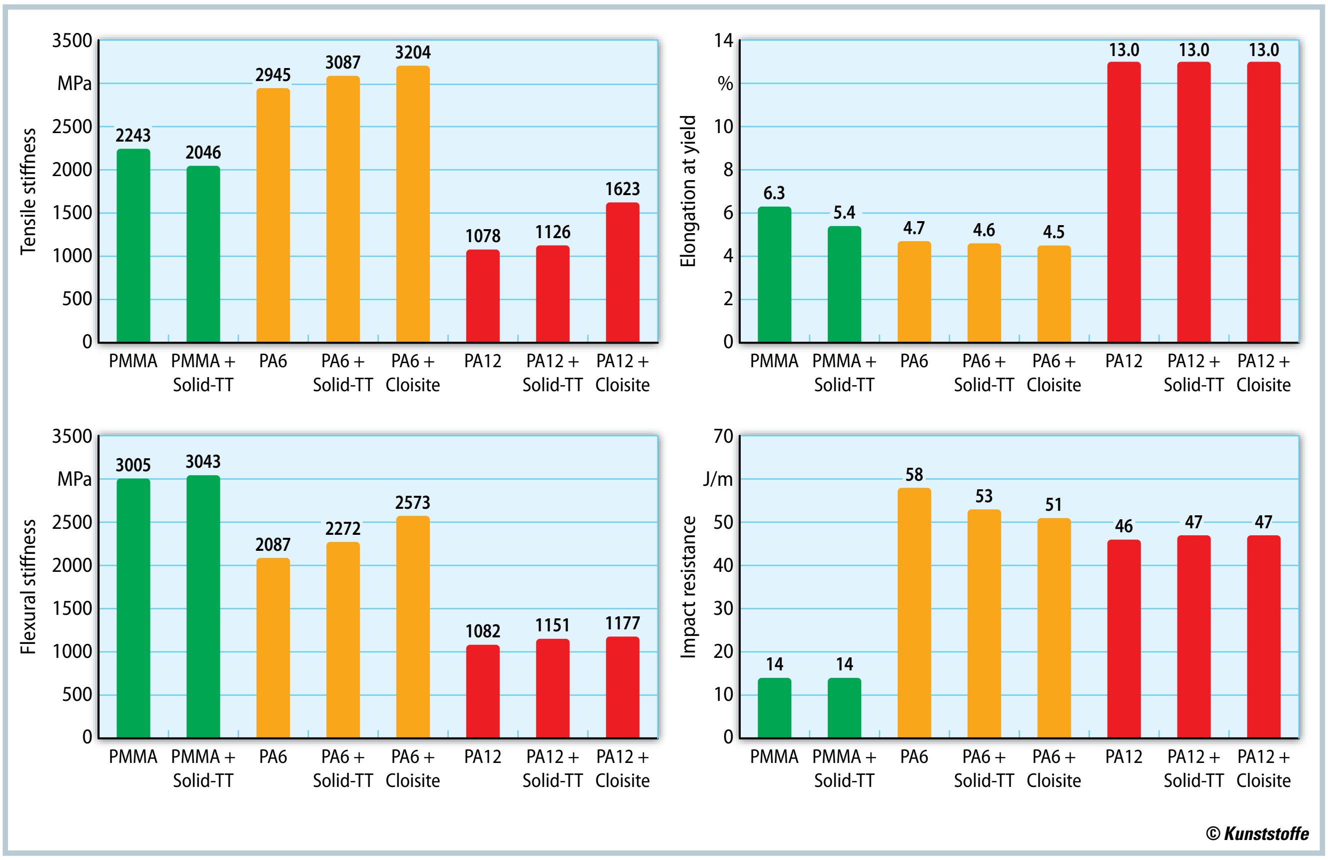

Fig. 4. Mechanical properties of PMMA, PA6 (Akulon K222-D) and PA12 (Rilsan AMNO) with organoclay additives (source: TenasiTech)

impact resistance of PMMA fell significantly (by 62%) with added Cloisite 30B, but only by 7% with Solid-TT (**Fig. 3**).

Summary

In the studies described here, the organoclay additive Solid-TT improved scratch resistance in polyamide, PMMA and PC. The comparison product Cloisite 11 did not achieve equivalent performance and in some cases even impaired appearance because its lower thermal resistance caused yellowing of the thermoplastics during processing. The mechanical properties of the composites with both additives proved to be similar and acceptable in comparison with the reference samples without additives (**Fig. 4**). Solid-TT did however considerably improve the properties of PA6 in comparison with unfilled PA6 subjected to the same processing. In PMMA, the additive brought about improved scratch resistance without loss of impact resistance, whereas Cloisite 30B in PMMA brought about a slight increase in scratch resistance but a dramatic decrease in impact resistance. In PC too, Solid-TT increased scratch resistance, but there was discoloration after compounding. Further studies with the addition of thermal stabilizers should thus be carried out. ■