COMBINING HARDNESS AND FLEXIBILITY IN COATINGS BASED ON NANOPARTICLE-FILLED HYPERBRANCHED POLYMERS

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ABSTRACT

The combination of hardness, scratch resistance and flexibility is a highly desired feature in many coating applications. The aim of this study is to achieve this through the introduction of a nano-clay filler in a polymer resin based on the hyperbranched polyester Boltorn H30. Smooth and uniform films could be prepared from both the neat and the nanoparticle-filled hyperbranched resin. XRD and TEM confirmed a mainly exfoliated structure in the nanocomposite films, which was also supported by DMA results. Furthermore, DMA measurements showed a 9-16 ºC increase in T_g, a higher storage modulus – both above and below the T_g – and indications of a more crosslinked network, for the clay-containing film. Conventional coating characterization methods demonstrated an increase in the surface hardness, scratch resistance and flexibility, with the introduction of clay, and all coatings exhibited excellent chemical resistance and adhesion.

KEYWORDS: Nanocomposites, hyperbranched polymers, montmorillonite, coatings, mechanical properties

INTRODUCTION

The combination of hardness, scratch resistance and flexibility is a highly desired feature in many coating applications. A potential route to achieve this aim is via the introduction of a nanoparticle filler into the polymer resin. The great interest for using nanoparticles to reinforce polymers emerged in the late 1980s when a research group from Toyota reported their findings regarding the possibility of building a nanostructure from a polymer and an organophilic clay, with dramatic property improvements [1]. Since then, improvements in mechanical properties, barrier properties, solvent resistance, thermal properties and optical properties have been reported for a variety of different polymers [2-4]. The employment of dendritic polymers in the preparation of nanocomposites, has been shown to promote the dispersion (exfoliation) of the nanoparticles and stabilize the exfoliated structure [5]. Furthermore, the unique features of dendritic polymers are also very favorable in coating applications; in addition to the large number of end-groups, offering versatile cross-linking possibilities, the globular structure of dendritic polymers enables a maintained low viscosity even at high molecular weights [6]. The aim of this study is to obtain a hard and scratch resistant coating, with maintained flexibility, through the introduction of a nanoparticle filler in a polymer resin based on the hyperbranched polyester Boltorn H30.

EXPERIMENTAL

Materials. The hyperbranched polymer Boltorn H30 was kindly supplied by Perstorp AB. The clay used is a natural montmorillonite, Na^+MMT, from the Cloisite® nanoclays series by Southern Clay Products, with a d-spacing of 11.7 Å according to SCP's x-ray results. Hexamethoxymethyl melamine (HMMM) was supplied by Becker Industrifärg AB, and epoxy-blocked p-toluenesulfonic acid (pTSA) was supplied by

Akzo Nobel Nippon Paint AB. TONE polyol 0301 was purchased from Union Carbide, and Texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) was purchased from Sigma-Aldrich.

Instruments and analyses. X-Ray Diffraction, XRD, analysis was performed with a PANalytical XPert Pro powder diffractometer, using copper-radiation, $CuK_{\alpha 1}$ ($\lambda \approx 1.5405981$Å). Transmission Electron Microscopy, TEM, analysis was performed on a Philips Tecnai 10, using an acceleration voltage of 80 kV. The TEM samples were UV-cured, cast in epoxy and cut with an ultramicrotome. The tensile properties of the coatings were measured on freestanding films with dynamic mechanical analysis (DMA), TA Instruments Q800. Conventional coating characterization methods: pendulum hardness was studied with a 299 Koenig pendulum hardness tester from Erichsen; pencil hardness tests were principally performed according to SIS 18 41 87 standard, using pencils manufactured by KOH-I-NOOR; scratch tests were principally performed according to ISO 2409 standard, using a multi-edge cutting tool and a brush, both manufactured by Erichsen; chemical resistance was analyzed through a MEK-rub test.

Nanocomposite preparation of Boltorn H30 and Na^+MMT. Boltorn H30 (19.7 g or 19.1 g) was added to a round-bottomed flask, equipped with a glass stopper, and preheated in an oven at 140 ºC until it melted, in order to break the hydrogen bonds in the material. Deionized water (150 ml) was added and the flask was put in an oil bath at 100 ºC and the mixture was kept under stirring. When a cloudy solution was obtained Na^+MMT (0.31 g or 0.92 g) predispersed in boiling deionized water (50 ml), was added and dispersed in the polymer solution under vigorous stirring. After one hour the temperature was reset to 50 ºC, the stopper was removed and the mixture was kept under maintained stirring until most of the water had evaporated. The resulting gel was transferred to a silicon rubber mould and dried in air at 50 ºC for four days and under vacuum at 50 ºC for another four days.

Coating preparation. Coatings with and without nanofiller were prepared in the same way. Boltorn H30 (with or without Na^+MMT) (1.95 g) was preheated and dissolved in methanol (3.8 ml). HMMM (0.45 g) and TONE polyol 0301 (0.60 g) were added, together with catalytic amounts of the epoxy-blocked pTSA and Texanol. Films were applied to glass substrates (for the pendulum hardness and MEK-rub tests), steel substrates (for the pencil hardness and scratch tests) and non-stick-coated steel substrates (to obtain freestanding films for DMA) and cured in an oven at 140 ºC for 20 min. The final Na^+MMT contents in the nanoparticle-filled coatings were 1 and 3 wt%, respectively.

RESULTS AND DISCUSSION

Coatings were prepared from neat Boltorn H30 (**Figure 1a**), and the nanocomposite of Boltorn H30 and Na^+MMT, using HMMM (**Figure 1b**) as crosslinker. The polyol TONE 0301 (**Figure 1c**) was added to increase the flexibility of the coating in order to facilitate the investigation of the influence of the nanofiller; since the nanofiller mainly affects the rubber plateau, the influence will be larger on soft and flexible materials. To avoid premature crosslinking, a blocked version of the catalyst pTSA was used, which is not activated until subjected to higher temperatures, i.e. in the curing oven. Texanol was added to facilitate the film-forming process, in order to obtain uniform and smooth films. Three different coatings were prepared, with 0, 1 and 3 wt% clay, respectively.

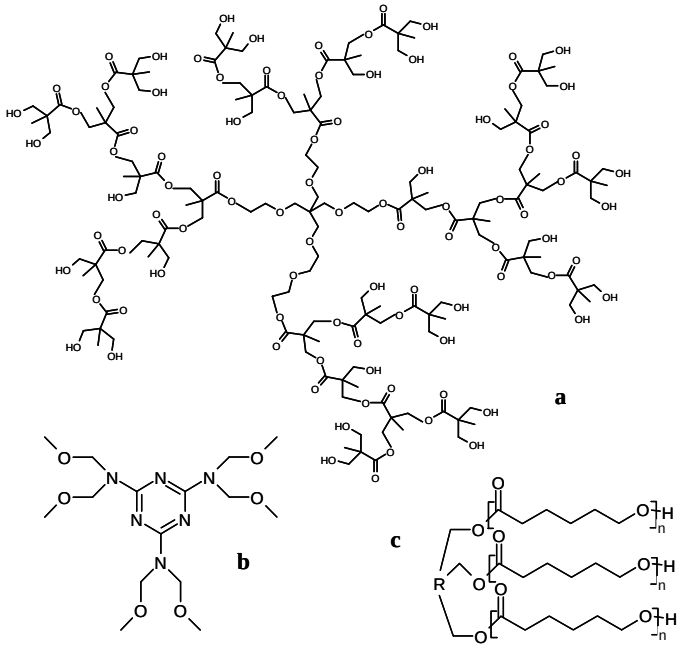

Figure 1. a) *Boltorn H30,* ***b)*** *HMMM,* ***c)*** *TONE polyol 0301, n≈2*

The dispersion of the clay layers in the nanofilled coatings was investigated with XRD and TEM. The large peak at 8° in the spectrum of pure clay, Na^{+}MMT, in **Figure 2** represents the regular distance between the clay layers. This peak cannot be seen in any of the spectra of the prepared nanocomposites, which is a strong indication that the regularity of the layered clay structure is broken, and that a mainly exfoliated structure is obtained both materials. The small peaks at 20° and 22° in the Na^{+}MMT spectrum can be used to verify that the clay content in the prepared nanocomposite materials is higher than the detection limit; these peaks represent smaller distances within the clay layers and would therefore remain even if the clay layers are dispersed, and an exfoliated structure is obtained. As can be seen, the peaks at 20° and 22° are visible in the spectra of both prepared nanocomposites, which confirms that the clay content is above the detection limit in these materials.

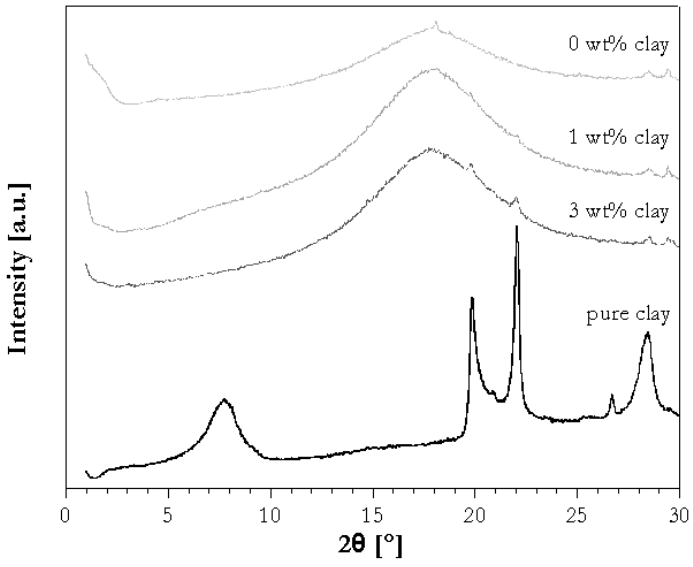

Figure 2. *XRD spectra of pure clay and the coatings with 0, 1 and 3 wt% clay.*

The results from TEM, shown in **Figure 3**, confirm the XRD results to a certain extent; both of the nanofilled coatings exhibit a mainly exfoliated structure.

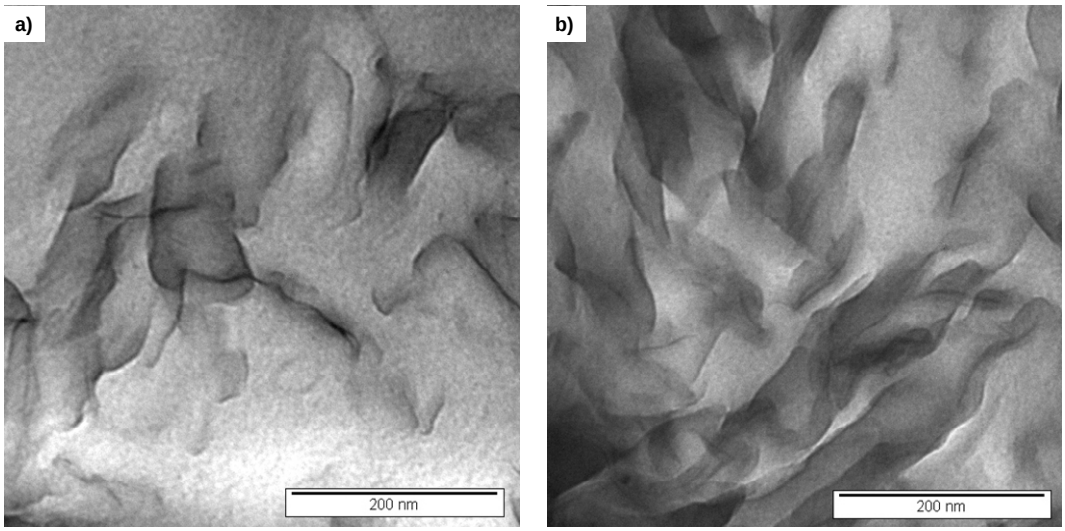

Figure 3. *TEM micrographs showing nanofilled coatings with a) 1 wt% clay and b) 3 wt% clay.*

The three different coating formulations, with and without clay, have been preliminary tested with respect to changes in mechanical properties induced by the introduction of the nanoparticle filler. DMA of freestanding films tested in tensile mode reveals a shift in the T_g from 48 ºC to 57 ºC and 64 ºC, for 1 and 3 wt% clay respectively, determined by the tanδ-peak value, **Figure 4a**. Furthermore, the tanδ curves are lower and slightly wider, indicating structures resembling a more crosslinked network. This implies that the clay interacts with the polymer network on a small scale, i.e. nanoscale, level; a macroscopic mixing of the filler would not give the same shift in T_g. Moreover, it is evident that the clay does not interact with the crosslinking chemistry in a detrimental way, although some chemical interactions probably occur. An increase in storage modulus for the clay-containing film both above and below the T_g is also seen, **Figure 4b**.

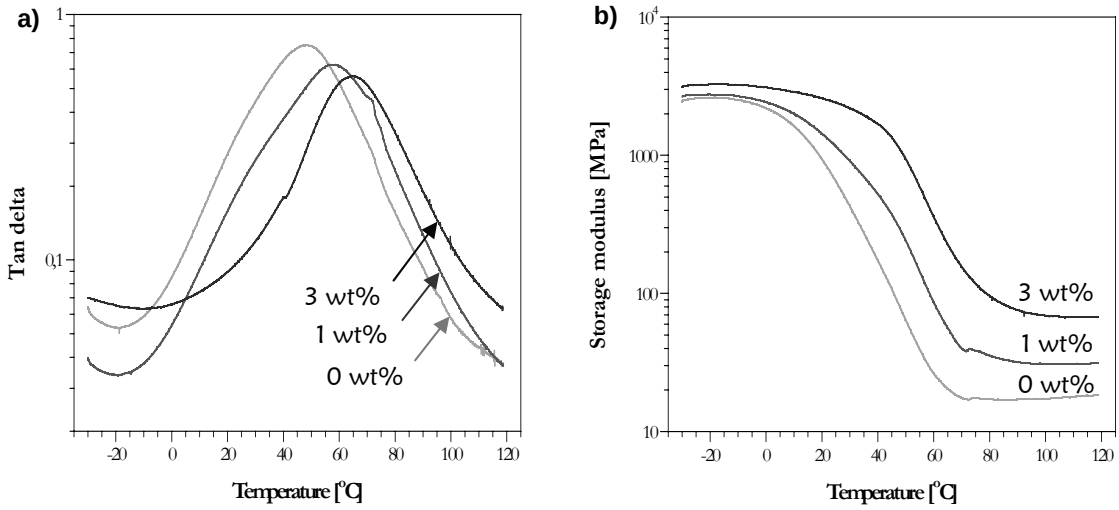

Figure 4. *DMA results showing a) storage modulus vs. temperature, and b) tan δ vs. temperature, of the prepared coatings.*

The results from the conventional coating characterization methods are shown in **Figure 5**. The results from the pendulum hardness test, which measures the surface hardness in combination with the surface friction, is in concordance with the DMA results; the nanoparticle-filled coating gave rise to a higher number of pendulum swings, indicating a harder surface. According to the pencil hardness test, the addition of clay had a pronounced positive effect on the scratch resistance, and with the scratch test it could be seen that the coatings all had good adhesion to the substrate. The aim of this project was to prepare hard coatings with preserved flexibility, but the Erichsen test actually showed a slight increase in the flexibility, with the addition of clay, which was better than expected. The chemical resistance of the coatings was evaluated using the MEK-rub test, and even after more than 200 rubs the films remained unaffected by the solvent; hence the coatings had very good chemical resistance.

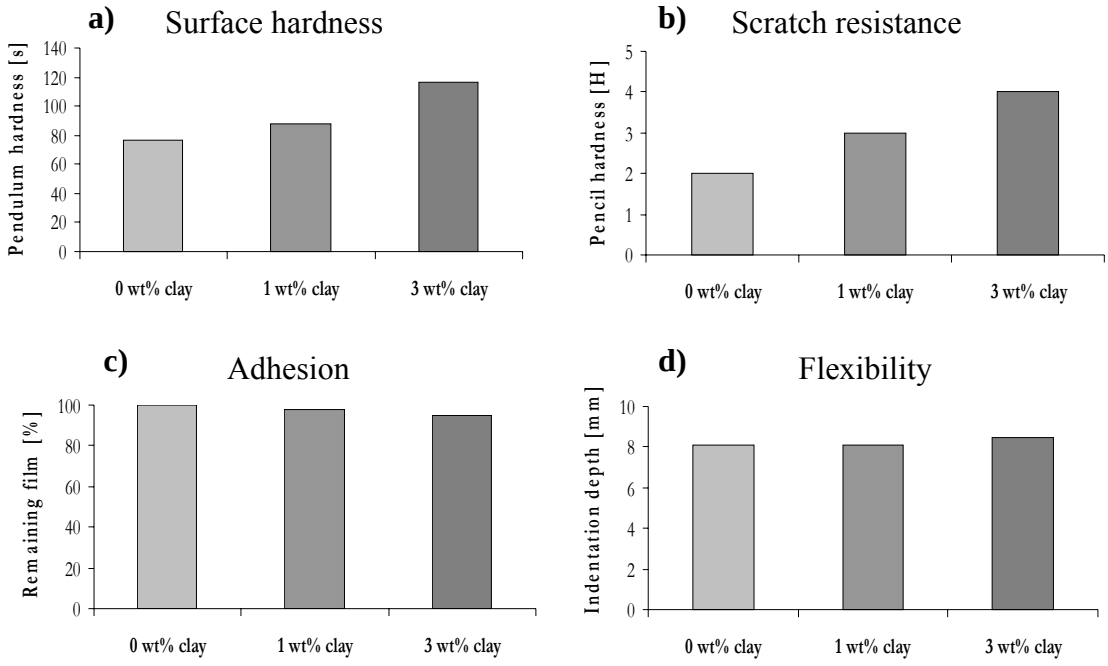

Figure 5. *Results from the conventional coating characterization methods a) pendulum hardness test, b) pencil hardness test, c) scratch test, and d) Erichsen ball test, denoted by the properties they measure.*

CONCLUSIONS

Smooth and uniform films could be prepared from both the neat and the nanoparticle-filled hyperbranched resins. According to x-ray diffraction (XRD) and transmission electron microscopy (TEM) the nanofilled coatings had a mainly exfoliated structure, and DMA also rendered indications of a nano-scale dispersion. Furthermore, the DMA showed a 9 and 16 ºC increase in the T_g, for 1 and 3 wt% clay respectively, a slightly higher storage modulus – both above and below the T_g,- and indications of a more crosslinked network, for the clay-containing film. Conventional coating characterization methods demonstrated an increase in the surface hardness, scratch resistance and flexibility, with the introduction of clay, and all coatings exhibited excellent chemical resistance and adhesion.

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