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SURFACE AND MECHANICAL PROPERTIES OF POLYPROPYLENE/CLAY NANOCOMPOSITE

Huge consumption of polypropylene in the industries like automotive motivates academic and industrial R&Ds to find new and excellent approaches to improve the mechanical properties of this polymer, which has no degradation effect on other required performance properties like impact resistance, controlled crystallinity, toughness and shrinkage. Nowadays, nanoparticles play a key role in improving the mechanical and surface properties of polypropylene. In this study, three compositions of polypropylene/nanoclay, containing 0, 2 and 5% of nanoclay were prepared in an internal mixer. For characterizing the nanoclay dispersion in polymer bulk, TEM and XRD tests were used. For scratch resistance testing, scratch lines were created on the load of 900 grain on sheets and SEM images were taken and compared with neat PP scratch image. Crystallinity and mechanical behavior were studied. The results showed that mechanical properties and scratch resistance of the composites were improved.

Keywords: nanocomposite, nanoclay, polypropylene, mechanical behavior.

Polypropylene (PP) is an important thermoplastic material because of its good processing ability, high strength, chemical resistance, and low cost [1]. It has been used as the material of choice for interior auto parts and other component applications. However, the surface of polypropylene and its copolymers are generally very susceptible to damage [2]. Beside the improvement of stiffness and strength of polypropylene, its scratch resistance improvement is critical.

A better understanding of the role of additives and fillers in the scratch behavior of thermoplastic polyolefins (TPOs) is needed for the maximum utilization of TPOs for automotive applications. A wide range of inorganic materials, such as glass fibers, talc, calcium carbonate and clay minerals have been successfully used as additives or reinforcement to improve the stiffness and strength of polypropylene, but scratch susceptibility has not been improved [3,4].

Nanocomposites are a new growing generation of polymer-composites, which can give us a good solution for this problem. Nanocomposites are able to play a magical role in the polymer industry [5,6].

Polymer nanocomposites are a new class of multiphase materials containing a dispersion of an ultrafine phase, typically in the range of 1-100 nm. Among the different nanoparticles, nanoclay has attracted significant attention because it provides two distinct opportunities for dispersion in the polymer matrix that include intercalation and exfoliation. These studies indicated that polymer nanocomposites exhibit enhanced strength, modulus, and flame retardancy that are not exhibited by the individual phases or conventional composites containing micrometer size particles or fibers [1,7-14].

Automakers such as Ford and General Motors Corp. are beginning to use nanocomposites, made by the conventional process, in nonstructural applications. For example, GM is using the material in the step-assist on the GMC Safari/Chevrolet Astro minivans [15].

In this study, scanning electron microscopy (SEM) is used to characterize the scratch patterns on the polymer surface, and other changes on mechanical properties of polypropylene were investigated.

EXPERIMENTAL

The polypropylene (PI0800) used in the experiments was a product of Bandar Imam Co. Nanoclay (Nanoline DK1) was provided by Fenghong Clay Chem. Co. (China). PP-MAH, as a compatibilizer (trade name Fusabond-MD353D) was purchased from Dupont Chem. Co.

An internal mixer (Haake HBI system 90, 300cc, fill factor 0.8) was used to prepare the required composites (Table 1). Initially PP-MAH and nanoclay were mixed with ratio of 2:1 and then PP was added to the mixer. The mixing temperature was kept at 180 °C, the rotation speed set at 100 rpm. The mixing time was 8 min. In order to prepare the film of desirable dimensions, 2.5 g of composite were pressed under 12 atm. at 220 °C for 5 min. The sample was then cooled to room temperature. Films with thickness of 1.5 mm were obtained.

Table 1: composition of the compounds

Compound	PP	Nanoclay	PP-gr-Ma
D1	100	0	0
D2	96	2	2
D3	90	5	5

The tensile properties were determined in accordance with ASTM D-638 using Instron 6025 tensile testing equipment. A Zwick 5102 impact tester was used for the measurement of notched impact strength according to ASTM D256.

Differential scanning calorimetry (DSC) curves were recorded on a DSC 2010 machine (TA Instruments, New Castle, DE, USA) to examine the thermal behavior of samples. Approximately 5 mg of each sample was used and the measurements of the samples were performed by heating from 20 to 200 °C at a rate of 10 °C/min under nitrogen atmosphere.

For the transmission electron microscopy (TEM) analysis, the specimen was microtomed to an ultra thin section of 70 nm thickness using an ultracryomicrotome with a diamond knife. The structure was observed under a Phillips CM 12.

Scratch resistance and hardness of the specimens were tested following the procedure previously described [16]. To evaluate the depth of the scratches, SEM investigations were done using a Cambridge S-360 instrument.

X-ray diffraction (XRD) data were collected on a Siemens D5000 XRD with a 2θ range of 1.2-12°.

RESULTS AND DISCUSSIONS

Mechanical properties

The tensile and flexural strength of the samples are shown in Tables 2 and 3, and the impact resistance is presented in Table 4. As can be seen from these results, the strength and modulus were substantially increased compared with the neat PP without significant variations in toughness or impact strength as measured by standard nothed Izod Test.

Beside the mechanical properties, XRD patterns of nanoclay D2 and D3 and have been achieved (Figure 1). Curve analysis for these three samples
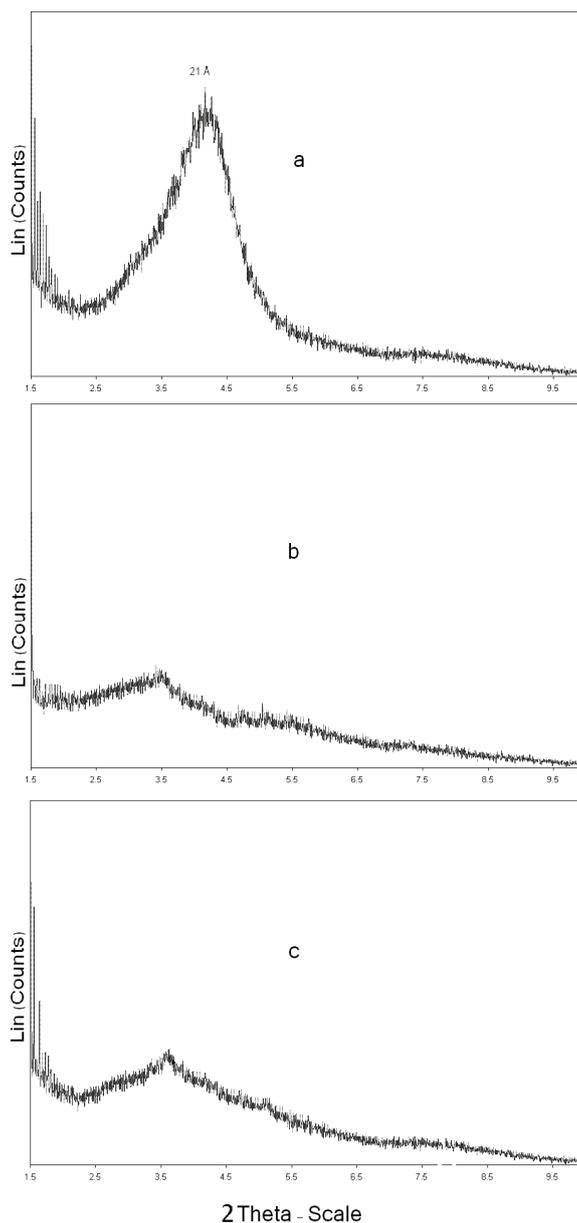
Table 2. Tensile strength test results of specimens

Speciemen	Width/thickness mm	Strain at peak %	Elongation at break mm	Peak stress MPa	Stress at yield MPa	Break stress MPa	Strain at yield %	Modulus MPa
D1	9.85/3.9	8.144	9.07	28.8	28.72	27.25	6.926	1100
D2	9.8/3.9	6.512	8.2	35.1	34.8	34.6	5.73	1450
D3	9.8/3.9	6.08	7.2	38.3	38.2	38	5.6	1720

Table 3. Flexural strength test results

Speciemen	Width/thickness, mm	Strain at break, %	Modulus, MPa	Strain at peak, %	Stress at yield, MPa
D1	10.55/9.95	0.105	1094.41	0.095	39.2
D2	9.9/9.65	0.081	1415.52	0.081	44.55
D3	9.9/9.65	0.076	1650.15	0.062	49.98

Table 4. Impact resistance results

Sample	D1	D2	D3
Impact resistance; Izod, N m/m	20.2	19	18

Figure 1. XRD Pattern of: a) nanoclay; b) nanocomposite D2; c) nanocomposite D3.

indicates that the interlayer platelet spacing of nano-clay is about 21 Å. Dissapearance of the d_{001} diffraction peak in D2 and D3 indicates the exfoliated structure of layers in nanocomposite. TEM images (Figure 2) were taken in order to obtain visible evidence of nanoclay layers in the polymer matrix.

Mechanical tests, TEM and XRD results and their comparison with other nanocmposite researches led us to conclude that D2 and D3 have mechanical properties expected from a nanocomposite [5,7,15]. The strong interaction in the polypropylene-clay system is responsible for significant changes in physical and mechanical properties [8].

Scratch resistance properties

In typical studies of scratch behavior of polypropylene, many factors such as filler type, additive, lubricant, impact modifier and surface morphology have been considered but in nanocomposites scratch studies, filer-matrix adhesion, positioning and orientation of nanolayers and polymer chains in the matrix have appeared as new factors [17]. Here we discuss these factors.

For characterizing the scratch patterns of sample surface, SEM images were taken (Figure 3) and the hardness of the surfaces was determined (Table 2). The crystallinity behavior of the samples was studied by DSC technique (Figure 4). There is a
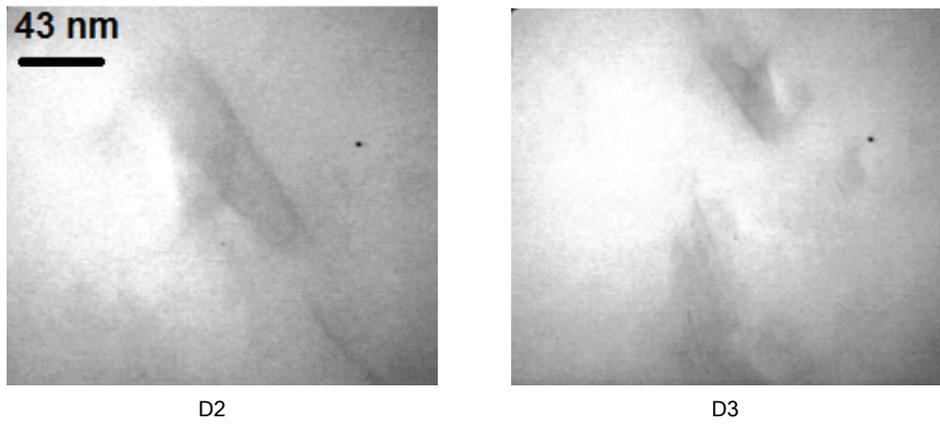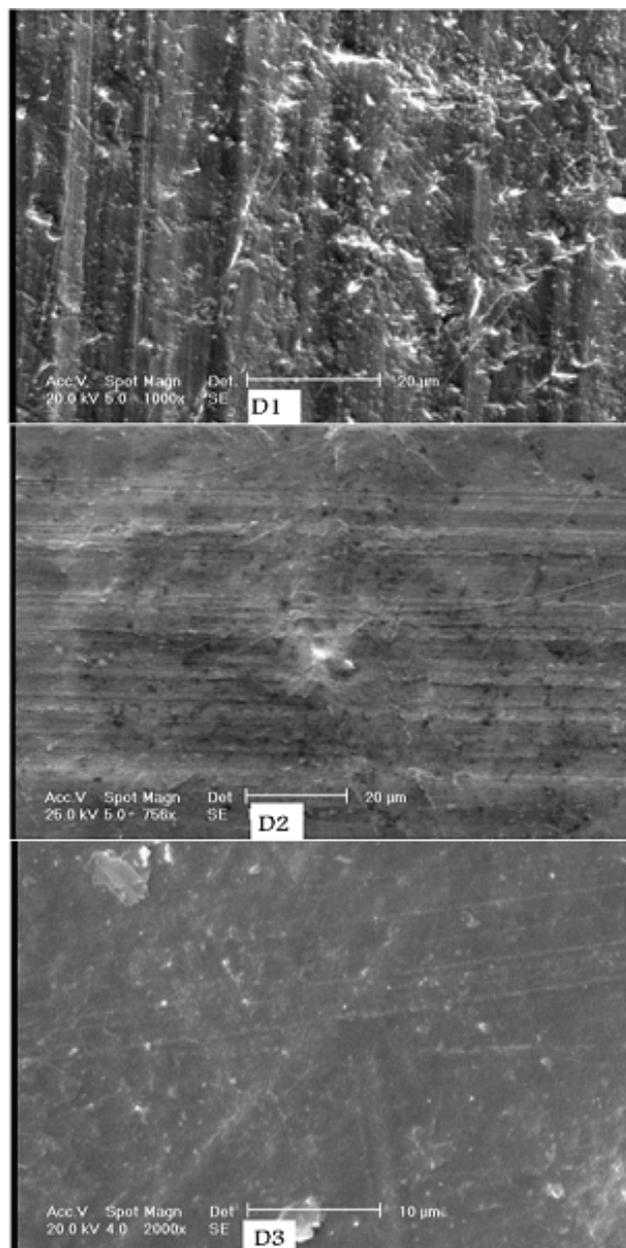
Figure 2. TEM Images of D2 and D3.

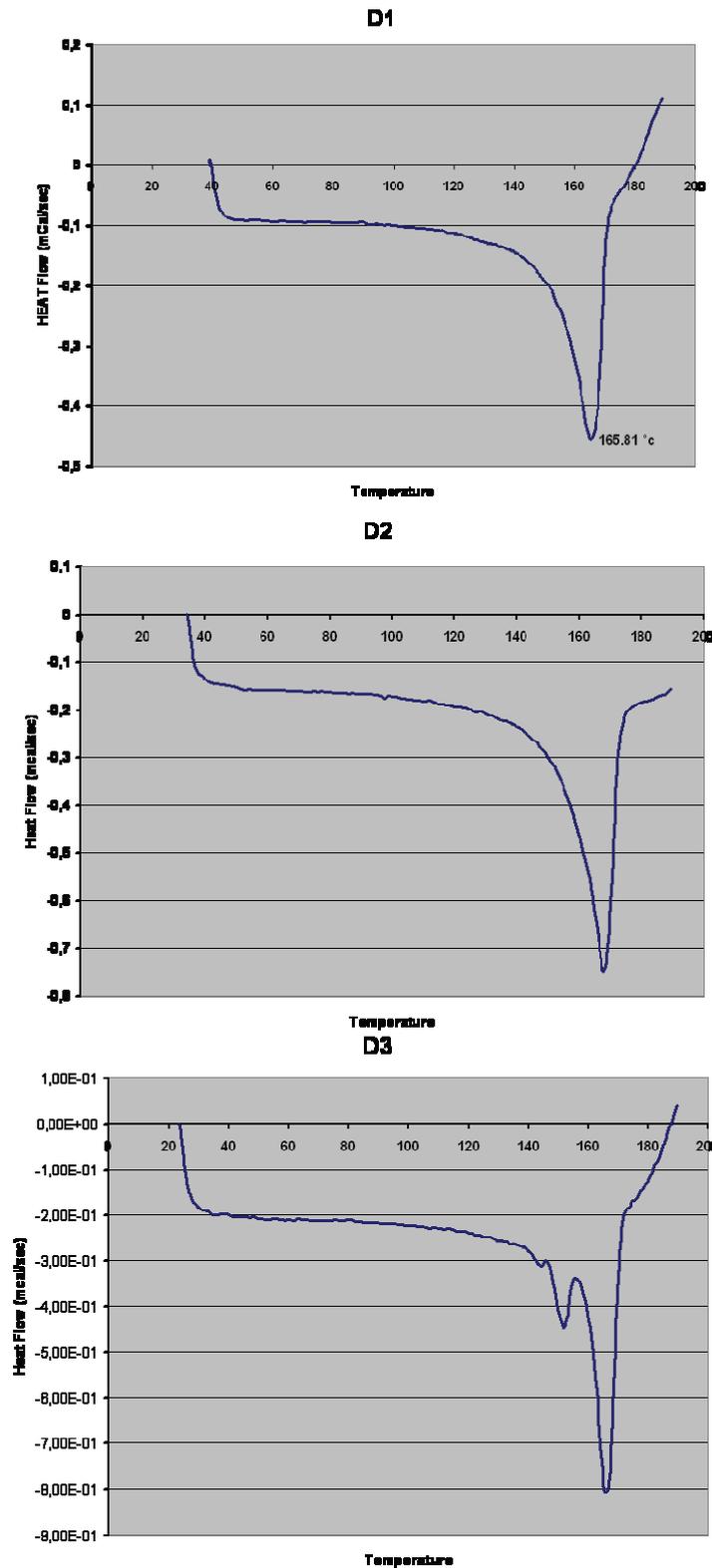Figure 3. SEM Micrographs of the scratch damage region at load of 900 g on the surface of each sample.

Figure 4. Differential scanning calorimerty (DSC) graphs of samples; T_{mD1} = 165.81 °C, T_{mD2} = 167.2 °C, T_{mD3} = 169.3 °C.

direct relation between the hardness and scratch resistance of polypropylene nanocomposites.

Under load, plastic deformation and stress whitening appear when scratch resistance is not high enough; this is due to the formation of voids, micro-crazing and debonding in polymer surface [3,17]. These fracture features of the surface lead to intense scattering of light from the surface and, in turn,

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increase the scratch visibility. We can visually compare the fracture features of the specimen surfaces, but for a comprehensive study, visibility factor of the surfaces, was used for the comparison of scratch lines in D1, D2 and D3.

To calculate the visibility factor, the gray value of every pixel in scratch image was determined using image analyzing software. The *G* function was as below:

G(image−pixel) = Gray value (0-255) in an image pixel (0 = black, 255 = white)

The fracture feature of the scratched surface of the polymer lead to increase of diversity of *G* on the image. So, the average value of *G* (image differentiation) was considered as a visibility factor:

$$\sum_{}^{n} G'(\text{image}-\text{pixel}) \Big/ n = \text{visibility factor } (n = \text{number}$$

of pixels in image)

The comparison in Table 5 suggested the sequence of visibility factor as D1 < D2 < D3. High visibility factor indicates weak scratch resistance. Therefore, the nanocomposite had more scratch resistance than neat polypropylene (Table 4) and D3 is fairly better than D2.

The improvement of scratch resistance and mechanical properties of polypropylene without more destruction in other required properties can be a revolutionary development in the auto parts industry.

Better bonding strength between the surfaces of nanoclay layers and the polymer is another important factor that determines the amount of fracture features

(scratch visibility). This bonding restricts the microcrazing and formation of voids and plastic deformation. The compatibilizer effect is considerable in better bonding strength. Also it could offset the positive effect from the increased clay dispersion and has shielding, plasticizing and miscibility effects [10].

For the rest of the paper, we describe the effective parameters, which have more influences on scratch resistance of nanoclay-filled polyolefin.

Polymer chains positioning near the surface

Layered structure of clay is determined as a key factor in improving the properties of polymers. Difusion of polymer chains to basal spacing of layers and its interaction with layer surfaces lead to a new structure in polymer bulk with lower entanglements of the chains (Figure 5). In this situation, the chains had a more elastic behavior when they were under stress. Also, the high aspect ratio of layers leads to damp the stress down and restrict the advance of stress to depth of polymer.

Crystallinity and nucleation

The crystallinity percentage and morphology strongly influence the scratch behavior and have direct effects on scratch resistance. Incorporating nanoclay and pure montmorillonite in the polymer matrix provides additional nucleation sites, thereby increasing the crystallinity.

In this study, the crystallinity of specimens increased according to $\chi_{cD3} < \chi_{cD2} < \chi_{cD1}$, in which χ_{cD3} is the percentage of crystallinity and is calculated as $\Delta H_{rev}/\Delta H^{p}$; where ΔH_{rev} is the endothermic melting enthalpy (Figure 4) and ΔH^{p} is the melting enthalpy of

Table 5. Comparison of visibility parameters and hardness of the specimens

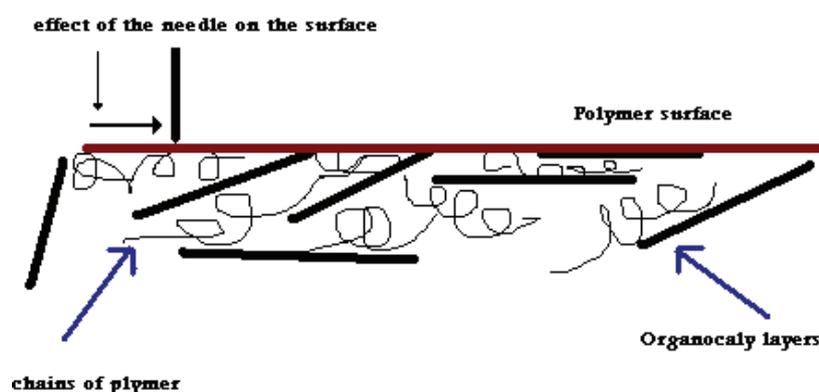| Specimen	Visibility factor (image differentiation)	Hardness (Shore D)
D1	143.1	71
D2	97.2	74
D3	70.9	77

Figure 5. Schematics of chains and layers positioning near the surface.

100% crystalline polypropylene [18]. High percentage of crystallinity increases the resistance of cracking and void creation under the scratch load. Nanoclay affects the crystallization behavior by increasing the equilibrium melting point of α and γ crystals indicative of thermodynamic interaction with the host matrix and is corroborated by the shift in the glass transition temperature [10].

Other parameters which may be considered

- Damping of stresses due to the layer structure of clay is the most influential factor in improving surface properties of D3.
- Quality of organic modification of the montmorillonite, lubricant and other surface modifiers.

CONCLUSION

Addition of nanoclay in small amounts (2 and 5%) improves the scratch resistance and mechanical properties of polypropylene. This case does not credit for typical additives such as talc; they increase susceptibility for plastic deformation in the polymer surface.

The layered structure of clay is an important factor that affects the damping of stresses. Because of the non-polar backbone of PP, a suitable compatibilizer is essential for the interaction of polypropylene and organo-layers.

The nanoclay/polypropylene nanocomposite is a potential material for automotive industry with a wide range of usages and it can be a choice of substitution for other polymers in automotives.

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NAUČNI RAD

POVRŠINSKE I MEHANIČKE OSOBINE NANOKOMPOZITA POLIPROPILEN/GLINA

Ogromna potrošnja polipropilena u automobilskoj industriji motiviše akademska i industrijska istraživanja i razvoj radi pronalaženja novih pristupa u poboljšanju mehaničkih osobina ovog polimera, koji nema degradacioni efekat na druge tražene performance, kao što su otpornost na udar, kontrolisana kristalnost, žilavosti i skupljanje. Danas, nanočestice imaju ključnu ulogu u poboljšanju mehaničkih i površinskih osobina polipropilena. U ovom radu, mikserom su pripremljene tri kompozicije polipropilen/nanoglina koje sadrže 0, 2 i 5% nanogline. Karakterizacija nanogline dispergovane u polimeru je izvršena pomoću TEM i XRD analiza. Za test otpornosti na grebanje, ogrebotine su formirane pri opterećenju od 900 linija po ploči, nakon čega su snimljene SEM slike i poređene sa PP scratch slikama. Takođe je proučavana kristalnost i mehaničko ponašanje kompozita. Rezultati su pokazali da su mehaničke osobine i otpornost na grebanje kod kompozita znatno poboljšani.

Ključne reči: nanokompoziti, nanoglina, polipropilen, mehaničko ponašanje.