

A Novel Core-Shell Polyacrylate/OMMT Nanocomposite Latex: Synthesis, Characterization And Its Application As A Coating Binder

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Abstract

Composite core-shell latex particles have an increasing importance in industrial applications especially for high performance waterborne coatings. They provide combined properties of different phase compositions for the final polymer which can also be enhanced by additives such as nanoclays. The present study describes the preparation of a hybrid polyacrylate/OMMT nanocomposite latex via two stage *in situ* emulsion polymerization with a low emulsifier content (1 wt.%) which is usually a challenge for the preparation of stable polymer/OMMT nanocomposite latexes. The obtained nanocomposite latex was stable and had a fine average size diameter of 151 nm with a very narrow size distribution. The copolymer films exhibited a well exfoliated structure observed by WAXD and TEM. Other polymer properties were investigated by FTIR, DSC, TGA, DMTA and rheological measurements. The results indicated that the addition of clay even in low amount (2 wt.%) yielded significantly improved mechanical and thermal properties of the final polymer. In addition, the nanocomposite latex was also applied on leathers as coating binder in a finishing formulation and the results of the performance tests revealed substantially increased rubbing and heat resistance whereas a slight decrease was observed at water vapor permeability of the coated leathers.

Keywords: Polymer/clay nanocomposites; Hybrid polymers; Emulsion polymerization; Latex stability; Leather Finishing

1. Introduction

Polymer/clay nanocomposites have been studied by researchers intensively and a large number of papers were already published. The interest in these nanocomposites is usually due to their unique properties like; increased modulus, thermal stability, inflammability, good barrier properties, chemical resistance and electrical conductivity, etc in comparison to the pure polymers and/or conventional composites. The exfoliation of clay platelets within the polymer matrix is the key factor for the enhancement of polymer properties. Among the preparation techniques of polymer/clay nanocomposites, emulsion polymerization has been used by various researchers effectively (Bhanvase et al. 2012; Lin et al. 2011; Herrera-Alonso et al. 2010; Zhang et al. 2009; Effenberger et al. 2009; Greesh et al. 2008; Lai et al. 2007). In

these studies both sodium montmorillonite (Na-MMT) and organically modified montmorillonite (OMMT) were used in nanocomposite preparations. Due to the hydrophilic nature of Na⁺-montmorillonite which is easy to disperse in water may result in intercalated nanocomposites because of insufficient interactions between the hydrophilic clay surface and the hydrophobic polymer chains. The use of organo-montmorillonites may provide better interactions between polymer and clay for obtaining exfoliated nanocomposites. However, too hydrophobic clays usually cause difficulties in emulsion polymerization when the stability of the latex is an important issue (Yilmaz et al. 2010).

In the last decade the composite latex particles are of great importance since their physical properties can be tailored (Khana et al. 2008). They are widely used in industrial applications, e.g. coatings, paints, adhesives, paper, textile manufacturing, etc (Kirsch et al. 2001; Henry et al. 1989; Gerli et al. 2003; Bertelo et al. 2002; Mendizabal et al. 1999; Wang et al. 2004; Zerafati et al. 2002; Ferguson et al. 2002). These materials usually have better properties than those of conventional polymers and/or blending of two or more polymer components. Such kind of latexes are commonly known as core-shell latexes and are usually made by emulsion polymerization in a two or multi-stage process where in the first step a seed latex (core) is formed from a monomer composition and in the second step another monomer composition is polymerized over the core to form the shell (Hidalgo et al. 1992; Ha et al. 2002). The polymers with two distinct phases usually have different compositions leading to different properties such as high and low glass transition temperatures, hydrophobicity, molecular weights, etc. which affect the properties of final polymer. There are many studies on the preparation of composite latexes in literature (Khana et al 2008; Pérez-Carrillo et al. 2007; You et al. 2011; Mu et al. 2009; Mizutani et al. 2006; Zhao et al. 2004; Chen et al. 2007; Qi et al. 2006; Reis et al. 2010; Zhang et al. 2012), however, fewer have been reported on the preparation of polymer/clay nanocomposite latexes with hybrid structures (Wang et al. 2009; Borthakur et al. 2010; Mirzzataheri et al. 2009). These studies also mostly focused on the encapsulation of clay via mini emulsion polymerization or stabilization of the latex particles via Pickering emulsion polymerization. Present study deals with the synthesis of a hybrid polyacrylate/OMMT nanocomposite latex via two stage seeded emulsion polymerization. The present approach used for the synthesis of nanocomposite latex provided many advantages for the stabilization of latex with low emulsifier amount, the well distribution of clay layers and thus the enhancement of mechanical and thermal film properties. The synthesized hybrid nanocomposite latex was also applied on leather as a coating binder in finishing and the coating performance was tested using official standard methods.

2. Materials and method

2.1. Materials

As clay material Nanomer® I.30E (Aldrich) a montmorillonite clay containing 25-30 wt.% octadecylamine as modifier was used in nanocomposite synthesis. Butyl acrylate (BA, ≥99%), tert-Butyl acrylate (tBA, 98%), Acrylamide (AAM), 2-Hydroxyethylacrylate (HEA, 96%), triethoxyvinylsilane (VTES, 97%) were supplied from Aldrich and used as monomers. The other necessary chemicals; sodium dodecyl benzene sulfonate as emulsifier (SDBS, C₁₈H₂₉NaO₃S, tech. grade), potassium persulfate (KPS, K₂S₂O₈, ≥99%) as initiator, sodium bicarbonate (NaHCO₃, ≥99.5%) as buffer and sodium hydroxide (NaOH, ≥99%) as a general alkaline were also supplied from Aldrich. All chemicals were used as received without any further purification. The polymerization reactions took place in a 3 necked 500 mL glass reactor equipped with a condenser, nitrogen pipe and a rubber septum for feeding. The reactor

was put in a water bath which was placed on a magnetic heater with a digital temperature control and the mixing of reaction medium was carried out with a magnetic stirrer.

Crust bovine upper leather was supplied from a regional tannery company (Sepiciler Inc. Co., İzmir-Turkey) and was used for leather finishing application. Other necessary commercial chemicals for finishing such as pigment, wax, aqueous nitrocellulose lacquer, surface modifier were supplied from Verbo Co. Inc. (İzmir-Turkey) and used in the formulation together with the nanocomposite latex.

2.2. Preparation of the hybrid polyacrylate/OMMT nanocomposite latex by two-stage seeded emulsion polymerization

OMMT clay (2 wt.% based on monomer mass) was mixed with the first phase monomers of BA and HEA overnight and ultrasonicated for 30 min prior to the polymerization. Selected amount of SDBS emulsifier, NaHCO₃, half of KPS initiator and AAm monomer were first dissolved in water and mixed in the reactor for 15 min. The pH of the reaction medium was arranged between 7-7.5 by dropping 0.5 M NaOH solution. After introducing 1/2 portion of I. phase monomers/OMMT mixture in the reactor to form a seed dispersion, the system was purged with nitrogen gas for 30 min to remove the dissolved oxygen from the reaction medium. When the temperature was reached to 70 °C the system was maintained for 60 min at 350 rpm to prepare the seed latex. The rest of I. phase monomers/OMMT mixture (1/2 portion of BA/HEA/OMMT) was dropped into the reaction medium within 1 h by injection through the rubber septum. After adding one quarter of KPS solution the system was reacted for another 60 min to form the core part of the nanocomposite latex. Subsequently, the second phase monomer mixture of tBA and VTES was dropped into the system within 90 min. The rest of the initiator solution (one quarter) was added in the reactor and the system was kept for 60 min. For completion of the reaction the temperature was raised to 80°C and the system was reacted for additional 1h. At the end the system was cooled down to room temperature and the nanocomposite latex was obtained with a total solid content of 20% and a conversion ratio over 95% (measured gravimetrically). The reference latex was also prepared under the same conditions without using O-MMT. The experiments were done in duplicates and average values were presented.

The copolymer films necessary for analysis were obtained by casting the emulsion on a glass substrate and drying at room temperature for 3 days and in oven at 70°C for 1 day.

2.3. Characterizations

A nanoZS model (Malvern Instruments UK) zetasizer instrument was used for the measurement of particle size and zeta potential of the latexes.

The IR spectra of the copolymer films were recorded with a Perkin-Elmer Spectrum-100 ATR-FTIR instrument by scanning in the range of 600-4000 cm⁻¹. The average interlayer spacing of OMMT before and after polymerization was investigated by a Philips PW 3710 Wide Angle X-ray Diffractometer (WAXD) (Cu-Ni radiation, $\lambda = 0.154$ nm). The distances between clay layers were calculated with Bragg's law: $2d \sin \theta = n\lambda$; where λ is the wavelength of the X-ray, d is the interspacing distance and θ is the angle of incident radiation.

For TEM investigation of the nanocomposite film ultrathin (60 nm) sections were cut, under liquid N₂, from a stained (RuO₄ vapor for 90 min) sample using an Ultracut UCT (Leica) ultramicrotome. Subsequently, the sample was examined by using a JEM 200CX (JEOL, Japan) microscope. The TEM micrographs were taken at acceleration voltage 100 kV, recorded on a photographic film and digitized with a PC-controlled digital camera DXM1200 (Nikon, Japan).

Elastic moduli the copolymer films were measured with a Rheometer Anton Paar MCR301 instrument equipped with dynamic mechanical analysis accessories at a constant frequency of 1Hz within -50 to 100 °C temperature range. Differential Scanning Calorimetry (DSC) thermographs were recorded with a Perkin Elmer Diamond DSC instrument at a heating rate of 10 °C/min under N₂ atmosphere from -70 to 100°C. The thermogravimetric behavior of the copolymer films was also investigated by a Perkin – Elmer Thermogravimetric Analyzer (TGA) with a heating rate of 20 °C/min under O₂ atmosphere from 30 to 500 °C.

2.4. Application of the nanocomposite latex and testing the performance of coating

For finishing application rectangular leather specimens (20 x 30 cm) were cut symmetrically from the parallel sides of the leather. The formulation of finishing mixture consisted of a pigmented coat and a top coat (Table 1). The coating layers were applied by a hand spraying gun with air pressure of 3 atm. After the application of each cross spray, the leathers were dried at 90°C in a drying tunnel for 3 min and hot plated at given intervals. The formulation was prepared as simple as possible for an easier evaluation of the effect of the nanocomposite binder on finish properties. The finished leathers to be tested by physical methods were conditioned according to the standard of EN ISO 2419 and the sampling was made according to EN ISO 2418. The efficiency of finishing applied on leathers was evaluated by the physical tests of; Flexing endurance (EN ISO 5402) which simulates the bending of leather product during daily use and evaluates the cracking of the film at bending region; Color fastness of leather to To and Fro rubbing (SLF 450) measures the resistance of the film to a moving felt on the leather surface and evaluates both the damage on finish layer and color transfer to felt; Color fastness of leather to ironing (SLF 458), a test which a metal finger moves on leather surface under specified pressure and speed at a temperature selected in the range of 80-240 °C and the resistance of the color of leather and finish layer to heat is evaluated; The water vapor permeability of the leathers was assessed by the official standard of EN ISO 14268:2002. The evaluation of all the tests related to color change was done according to the Grey Scale Standard (IUF 131-132) which gives a rating between 1 to 5 (5: means no color change, and 1: means failure).

Table 1. The coating formulation applied on the leathers

Components	<u>Application Steps</u>		Descriptions
	Basecoat (A)	Topcoat (B)	
Water	35 g	20 g	Spray A x 3 times
Pigment	10 g		Hot plate 70°C/100 bar
Wax	5 g		
Latex copolymer	30 g		Spray A x 4 times
Aqueous NC Lacquer		10 g	
Silicone Surface Modifier		0.5 g	Spray B x 1 time
			Hot plate 90°C/70 bar

3. Results and discussion

3.1. Stability of the nanocomposite latex

The stability problem caused by organophilic clays in emulsion polymerization is usually due to the high hydrophobic character of the clay modifier which causes difficulties for the transportation of clay layers from monomer droplets into the aqueous phase during the nucleation period in a conventional emulsion polymerization (Yilmaz et al. 2010, 2012). This usually results in coagulation or increased coagulum yield when relatively low amount of emulsifier is used (0-8 wt.%). This stability problem can be encountered especially when the ratio and/or the hydrophobicity of clay is high.

In the experiments the choice of some monomers and clay type, and also some design parameters of the polymerization system were made in order to increase the stabilization of nanocomposite latex together with promoting the enhancement of final polymer properties. More particularly, a moderately hydrophobic organo-montmorillonite which had 25-30 wt.% octadecylamine modifier was preferred as clay material and used at 2 wt.% based on total monomer mass. In the experiment the addition of OMMT was made during the core part formation of the latex and this brought some advantages. Because the solid content of total system was lower during the first phase formation and the introduction of clay in the system were made within a period, the risk of coagulation was decreased and the polymerization was performed with a better control. Moreover, the total emulsifier amount used in the synthesis was introduced into the system at the beginning of reaction, therefore during the clay addition a maximum stability was provided. During the formation of second phase, the clay layers should have been inside and/or surface of the core phase, thus after the completion of the second phase a better encapsulation of clay layers could be provided. Consequently, at the end of reaction a coagulum free nanocomposite latex was obtained successfully containing 2 wt.% OMMT and 1 wt.% emulsifier (SDBS) via two stage seeded emulsion polymerization.

3.3. Particle size and zeta potential of the nanocomposite latex

From the dynamic light scattering analysis the average particle size diameter of the reference latex was measured as 142 nm while the nanocomposite latex had a very slightly increased particle size diameter of 151 nm (Table 2). This increase was possibly due to the existence of clay layers; however, the increase was very slight and negligible. The particle size distributions of the samples were shown in Fig. 1. Both the latexes exhibited only one narrow peak indicating very homogenous distributions. Accordingly, the polydispersity index value (PDI) of reference latex was 0.09 while the nanocomposite latex had a PDI value of 0.08.

The zeta potential (Z.P.) measurements showed that the reference latex had a value of -28 mV while the nanocomposite latex had a slightly decreased Z.P. value of -32 mV indicating that both latexes were electrostatically stable and coagulum free (Table 2).

Table 2. Z-average diameter, polydispersity index (PDI) and zeta potential (Z.P.) values of the reference and nanocomposite latex

Sample	Z-average Diameter (nm)	Polydispersity Index (PDI)	Zeta Potential (mV)
Reference latex	142	0.09	-28
Nanocomposite latex	151	0.08	-32

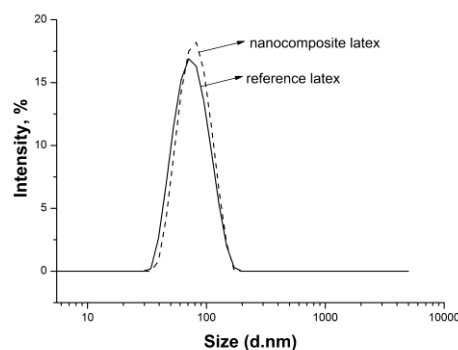


Figure 1. Particle size distributions of the reference and nanocomposite latexes

3.4. IR spectrum of the nanocomposite

FTIR analysis of the samples (Fig. 2) showed the main absorbance peaks at 1065, 1148, 1367-1450, 1727 cm^{-1} which were attributed to the stretching of C-O-C, OR-C-C, C-H bending of CH_2 , C=O stretching of the acrylic components of BA-tBA-AAm-HEA, respectively. The other common peaks of 2874, 2934 and 2960 cm^{-1} could be due to the *sym* C-H stretching of CH_2 , *asym* C-H stretching of CH_2 , *asym* CH_3 stretching of BA-tBA-HEA. The specific bands of 1392 and 1687 cm^{-1} could be assigned to the $-\text{CH}_3$ *sym* bending of VTES and C=O stretching of CO (ν) amide I band of AAam, respectively. The broad band with low intensity observed between 3100 and 3700 cm^{-1} could be due to the *sym* and *asym* N-H vibrations of AAam, $-\text{OH}$ stretching of HEA. The specific bands of VTES due to Si-O-C group normally appearing between 1060 and 1110 cm^{-1} were not clear due to its low content and overlapping on the absorption bands of acrylic monomers within the same range. A similar case was observed also for OMMT clay. The IR spectrum of the clay showed that the main absorbance peak appeared at 1030 cm^{-1} due to the stretching of Si-O-Si groups. However, in the spectrum of nanocomposite no individual peak was observed for OMMT due to the overlapping on the absorbance peaks of 1035 and 1065 cm^{-1} of the acrylic monomers. On the other hand, an increase in the peak intensity in these bands was observed due to the existence of clay (Fig. 2b). In addition, the characteristic peak of C=C at the stretching band of 1645 cm^{-1} due to the residual monomer was not observed in all spectra.

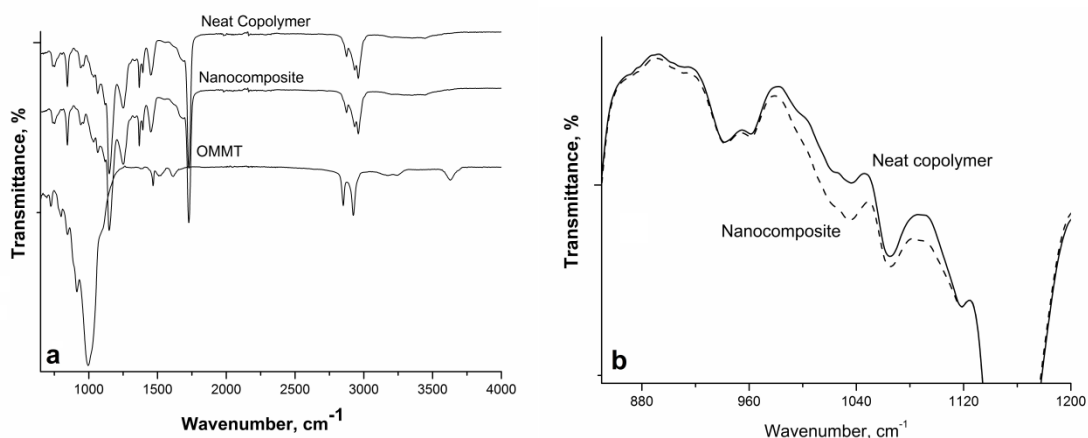


Figure 2. FTIR spectra of; a) Composite polymer films and OMMT, (b) expanded peak area at 1030-1065 cm^{-1}

3.5. WAXD and TEM investigation of the nanocomposite film

The WAXD patterns of the nanocomposite, neat polymer and OMMT clay were given in Fig. 3 (left). The main reflection of OMMT appeared at around 4.14° 2θ degree which corresponded to a d-value of 2.13 nm. However, there was no reflection peak in the diffractogram for the nanocomposite indicating a complete exfoliation state.

The TEM image of the nanocomposite film was given as Fig. 3 (right) where dark structures represent the clay layers and lighter regions the polymer. From the image the individual clay layers distributed unevenly in the polymer matrix were observed which verified the exfoliated structure of the nanocomposite.

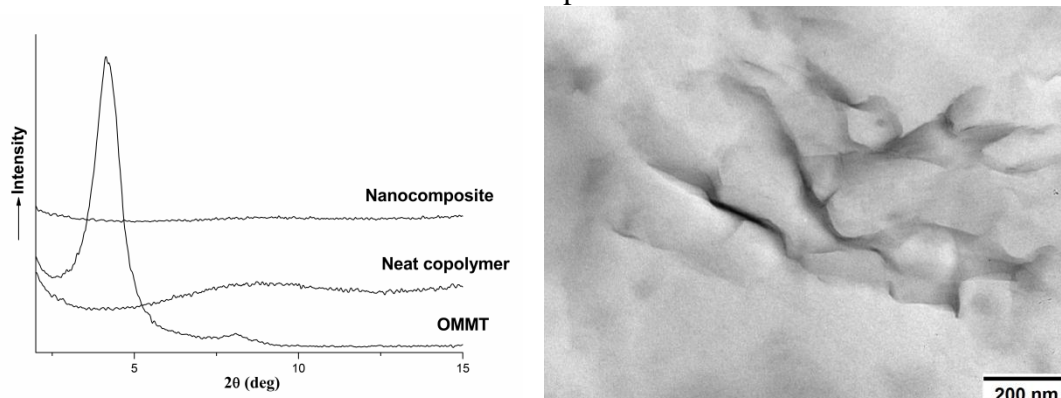


Figure 3. WAXD patterns of the copolymer, nanocomposite and OMMT (left), TEM image of the nanocomposite film (right)

3.6. Thermal and mechanical properties of the nanocomposite

DSC curves of the copolymers with and without clay showed two distinct and clear phase transition points (Fig. 4a). The copolymer without clay had T_{g1} at -43°C and T_{g2} at around 48.3°C while the nanocomposite showed transition temperatures at -45 and 46.5°C which were slightly lowered. Normally the existence of clay layers in polymer matrix are known to increase the T_g values since they confine the movement of polymer chains. This situation usually occurs in highly filled and/or intercalated nanocomposites. However, in the present case the clay addition didn't increase the T_g s, probably due to the exfoliation state of clay layers which did not hinder the molecular motion of polymer chains. Infact this is a more desirable situation for obtaining nanocomposites without changing T_g where elastic and flexible polymers are desired.

Fig. 4b shows the TGA curves of both the reference copolymer and nanocomposite films. In the graph two decomposition regions were observed for both samples due to the existence of two distinct polymer phases. In the early stages of decomposition process both samples showed similar behavior and onset temperatures; however, after 10 wt.% mass loss the decomposition temperatures of the nanocomposite shifted to higher values. For instance, the temperature at 10 wt.% mass loss was 255 and 257°C for the neat copolymer and nanocomposite, respectively; however, 20 wt.% mass loss temperature of the neat copolymer was shifted from 294°C to 344°C and for 50 wt.% mass loss from 395 to 410°C for the nanocomposite. Moreover, the final mass of the neat copolymer was found to be 1.4 wt.% whereas the nanocomposite had a final mass of 22.5 wt.%. Therefore, the addition of 2 wt.% OMMT increased remarkably the thermal stability of the polymer.

The elastic moduli (E') of copolymer films as function of temperature were given in Fig. 4c. Similar to the TGA results two phase transitions were also observed for E' curves. However, with the usage of 2 wt.% OMMT, the increase in elastic modulus of the

nanocomposite in respect to the neat copolymer was drastic and higher values were obtained (almost 10 times higher for all range). As an example, E' value of neat copolymer film at room temperature (20°C) was found to be 3.3 MPa while the nanocomposite film had an E' value of 28 MPa.

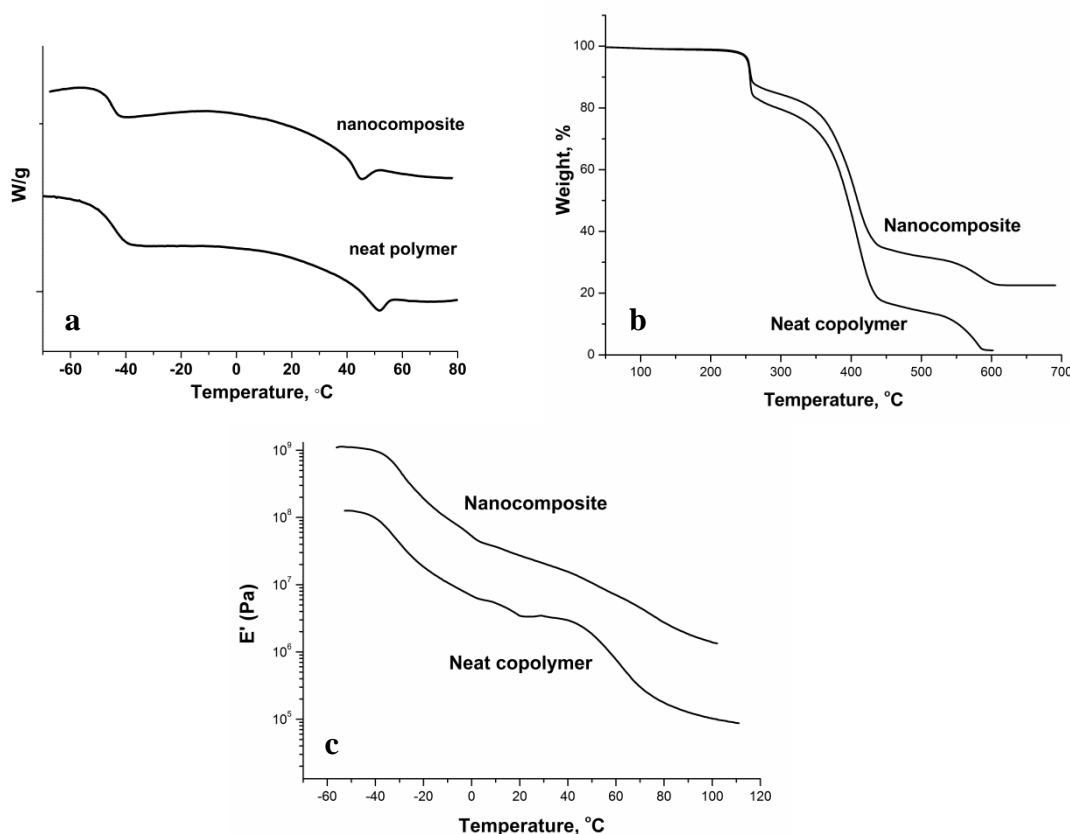


Figure 4. DSC (a), TGA (b) and DMTA (c) curves of the nanocomposite in comparison with the neat copolymer

3.8. Finishing performance of the nanocomposite latex

After the application it was observed that both leathers had glossy and natural appearance and there was no impairment on the appearance due to the existence of clay.

The flexing endurance of the leathers (EN ISO 5402) for all samples was perfect after 100.000 times of flexing. This showed that the hard phase of the copolymers didn't impair the elastic character of the copolymer films. Moreover, the flexibility of the finishing layer was also not affected negatively by clay incorporation.

The rub fastness results of the finished leathers were given in Table 3. The leather coated with the neat latex showed a failure for finish layer after 1000 rubs as indicated with the value of 1. The coloration of the felt was also higher having a grey scale value of 2/3. However, with clay incorporation the rub fastness values of the leather increased remarkably where the color change of the leather and the felt was much lower with a rating of 4 in grey scale. In Fig. 5 the photographic images of the leathers after x1000 rubs were shown and the effect of clay was very obvious.

In Table 3 it was also given the results of ironing resistance of the leathers. The ironing resistance test lets us to assess the behavior of leather surface color on exposure to a hot iron,

as for instance in crease removal in shoe manufacture or ironing in garment manufacture. Meanwhile, it also gives information about the heat resistance of the finishing film on the leathers. The failure temperature of the finish layer against ironing was found to be between 120-140 °C for the leather coated with the neat latex. However, the leather coated with nanocomposite latex exhibited a maximum ironing temperature of 180-200°C which was increased remarkably due to clay addition.

The leather coated with the nanocomposite latex showed slightly decreased water vapor permeability in comparison to the leather finished with the neat latex (Table 3). This was an expected situation since dispersed platelets of the silicate sheet result in a tortuous pathway for the permeating molecules through the polymer matrix (LeBaron et al. 1999; Yano et al. 1993). However, due to the low clay content (2 wt.%) the decrease in water vapor permeability of the leather was slight (decreased by 12%) and the breathability of the leather was not affected significantly.

Table 3. The results of the performance tests applied to the finished leathers

Leather Sample	Flexing Endurance x100.000 times	Fastness level x1000 rubs (dry)		Ironing Temperature (°C)	Water Vapor Permeability (mg.cm ⁻² .h ⁻¹)
		Leather	Felt		
Without clay	Excellent	1	2/3	120-140	9.58
With clay	Excellent	4	4	180-200	8.44

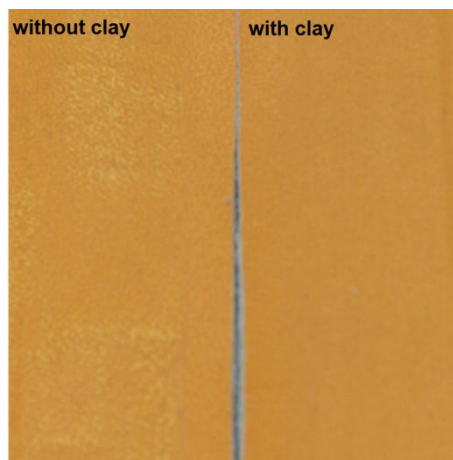


Figure 9. Photographic images of the leather samples after x1000 of rubbing; a) without clay, b) with clay

4. Conclusions

A hybrid nanocomposite latex was synthesized via two stage seeded emulsion polymerization where poly(BA-AAM-HEA)/OMMT was served as first (core) phase and poly(tBA-VTES) as second phase. The selection of the monomers and clay, polymerization conditions and gradually addition of OMMT dispersed in first phase monomers helped to increase the stability and control of the system. The overall results of the study revealed that even with a low percentage of clay loading (2 wt.% based on total monomer mass) it was possible to obtain a stable nanocomposite latex with significantly enhanced mechanical and thermal polymer film properties which were also in accordance with the performance of the coating obtained by its specific application. The synthesized nanocomposite latex was found

to be proper for industrial applications as a waterborne acrylic binder for protective coatings, especially for leathers.

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