EXPERIMENTAL INVESTIGATION OF MECHANICAL PROPERTIES OF STARCH/NATURAL RUBBER/CLAY NANOCOMPOSITES

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This paper seeks the effects of operating variables on mechanical properties of starch/natural rubber/clay nanocomposites including tensile strength and modulus. The variables were natural rubber type, clay, glycerol and natural rubber contents. The experiments were carried out based on the design of experiments using Taguchi methods. Nanocomposites prepared with modified natural rubber indicated a mechanical improvement in the properties in comparison with unmodified natural rubber. It was also observed that increases in tensile strength and modulus would be attained for nanocomposite samples with 3%, 10% and 10% (by weight) of clay, glycerol and natural rubber loading, respectively. The clay intercalation and morphology of the samples was examined by X-ray diffraction (XRD) pattern and scanning electron microscopy (SEM), respectively.

1. Introduction

Starch-based materials originally attracted a great deal of interest because of their low cost, real biodegradability, and renewable origins [1]. The thermoplastic starch (TPS) is obtained after disruption and plasticization of starch macromolecules by heating in presence of water or other plasticizers such as glycerol. The products made from TPS are however water sensitive and would present inferior mechanical and physical properties. The mechanical weaknesses of these materials also can be usually improved by incorporation of an inorganic reinforcing material including montmorillonite (MMT) [2-4]. Thermoplastic starches have being also successfully blended with other suitable polymers to improve their mechanical properties and to reduce the dependence of their behavior on water content [5,6]. One of these polymers is natural rubber (NR, cis-1,4-pol`yisoprene). The natural rubber grafted with the hydrophilic poly dimethylaminoethyl methacrylate (DMAEMA) has proven to be an efficient compatibilizer to obtain blends of plasticized starch and natural rubber with useful properties [7,8].

The various processing methods used to prepare starch-based nanocomposites cause different filler distribution and exfoliation of the clay layers [9,10]. Many authors have investigated the effects of clay content on physical and mechanical properties of starch/clay nanocomposites [8,10-12]. The ultimate properties could be influenced by the factors including the type of natural rubber [8] and the glycerol content [13-15]. In our recent work [16] we mapped the effects of some factors on the modulus of starch/clay nanocomposites and we optimized the mechanical properties of these materials. Although there are, many papers recently published on the starch/clay nanocomposites; there are a few reports available regarding analysis of the effects of parameters on the physical and mechanical properties of starch/natural rubber/clay nanocomposites.

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The Taguchi experimental design method is a statistical approach that reduces the number of experiments necessary for investigating the effects of various parameters on the product quality and/or quantity. There is no report available regarding application of experimental design for comparative analysis of the effects of operating variables on the mechanical properties of starch/natural rubber/clay nanocomposites.

In this study, the influences of natural rubber type (A), clay content (B), glycerol content (C) and natural rubber content (D) on the tensile strength and modulus of starch/natural rubber/clay nanocomposites prepared via melt extrusion method have been statistically investigated by using Taguchi experimental design approach.

2. Experimental

2.1. Materials

The used matrix polymer in this study was cornstarch with the amylose content of 28 wt% (Glucozan Co., Ghazvin, Iran). Natural rubber latex (stabilized with ammonia) from a local producer was used. Stearic acid and glycerol (about 87% purity) were obtained from Merck KGaA, Darmstadt, Germany. Cloisite®Na+ (MMT) as untreated montmorillonite was purchased from Southern Clay Products (USA) and was used as received. Oxidized PE homopolymer, A-C® 316, from Honeywell International Inc. (Morristown, NJ, USA) were used as lubricants during processing. Dimethylaminoethyl methacrylate (DMAEMA), cumene hydroperoxide (CHP), and tetraethylene pentamine (TEPA), all reagent grade chemicals from Sigma–Aldrich Co. (St. Louis, MO, USA) were used as received.

2.2. Design of experiments

The first important step in design of the experiments is the proper selection of factors and their levels. In this study, four main factors: natural rubber type, clay, glycerol and natural rubber contents were considered in three levels (Table 1). The factors and their levels have been selected according to a literature review on previous publications [8-11, 13-17], the practical aspects, and some screening experiments. For Taguchi-design of experiments with four factors, a standard L_9 orthogonal array was employed as shown in Table 2 [18]. Each row of the matrix represents one run at specified condition. In order to avoid the systematic bias, the sequence in which these runs were carried out was randomized [18,19].

Table 1. Selected factors and their respective levels

Factors	Symbol	level 1	level 2	level 3
Natural rubber type	A	unmodified	modified	-
Clay content (wt. %)	B	0	3	6
Glycerol content (wt. %)	C	10	20	30
Natural rubber content (wt. %)	D	0	10	20

The signal-to-noise ratio (S/N) is used as a transformed response in the Taguchi method to indicate the magnitude of changes in response due to variations of controlled factors respect to that of errors. In this work, the tensile properties were used in the response calculations. In order to maximize the tensile properties, the following S/N formulation is used (Roy, 2001):

$$S/N = -10 \times Log \left(\frac{1/y_1^2 + 1/y_2^2 + \ldots + 1/y_n^2}{n} \right) \tag{1}$$

In which y is the experimental measurement of the tensile strength or the modulus and n is the number of samples per trial. Larger S/N ratio is desired for optimization of responses.

Table 2. Taguchi L₉ orthogonal array of designed experiments.

Trial	Factors			
	A	B	C	D
1	unmodified	0	10	0
2	modified	0	20	10
3	unmodified	0	30	20
4	unmodified	3	10	10
5	unmodified	3	20	20
6	modified	3	30	0
7	modified	6	10	20
8	unmodified	6	20	0
9	unmodified	6	30	10

2.3. Preparation of modified natural rubber

The grafting procedure of DMAEMA onto NR was performed as described by Lamb et al. [20]. Natural rubber latex (324.32 g), DMAEMA (12.10 g), CHP (0.46 g), and 2.5 wt.% ammonia solution (154 g) were combined and agitated with a low shear impeller at approximately 200 rpm under a nitrogen atmosphere over a period of 1 h to allow the partitioning of CHP into the rubber particles. TEPA (0.62 g, as a 10 wt.% solution in H2O) was then added for over 1 h, at 5 min intervals, to initiate polymerization. The system was cooled in an ice/water bath for the first 8 h of reaction before gradual warming to room temperature and allowed to continue reacting for 16 h to obtain the modified latex.

2.4. Preparation of thermoplastic starch/natural rubber/clay nanocomposites

Starch/natural rubber/clay nanocomposites were prepared via melt extrusion technique. For the first step, the cornstarch, clay, and natural rubber (modified or unmodified) were combined in a high speed mixer according to the corresponding run of experiments. In this step glycerol as a plasticizer was added drop-wise during the mixing at 600 rpm, once all glycerol had been added, mixing continued at 1800 rpm for 10 min to access the uniform dispersion.

In the second section, starch nanocomposites processing was carried out in a co-rotating twin-screw extruder with screw diameter of 18 mm, and L/D ratio of 30. The extruder temperature profile from feed zone to die was 65, 70, 80, 90, 105, and 120 °C. The extrusion of each formulation was duplicated to ensure reproducibility.

2.5. Characterization of nanocomposites

X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) using CuKα radiation (40 kV, 40 mA and λ=0.154 nm). Samples were scanned at 1˚/min in the range of 2θ = 2–10˚. The basal spacing of the silicate layer, $d_{(001)}$, was calculated using the Bragg's equation ($n\lambda = 2d \sin \theta$), where θ is the diffraction angle and λ is the wavelength.

Tensile properties were performed on a 5500 R Instron testing machine, operated at 50 mm/min. Five specimens were tested for each sample, after a four-week period of conditioning at 25 ºC and 53% relative humidity (RH). The specimen shapes and the operating conditions were in accordance with the ASTM D 638 standard.

A JSM840A scanning Electron Microscope (SEM) was employed for microscopic observation of morphology of nanocomposite films.

3. Results and discussion

3.1. XRD data of nanocomposites

A characteristic diffraction peak is appeared at $2\theta=7.96°$ for MMT corresponding to gallery spacing of 1.11nm. The XRD data for nanocomposite films prepared at different conditions are presented in Table 3.

Table 3. XRD results of samples.

| Trial | XRD data | |
	2θ of the peak (°)	Δd (nm)
1	6.44	0.26
2	5.85	0.40
3	7.18	0.12
4	6.05	0.35
5	6.40	0.27
6	4.60	0.81
7	5.13	0.61
8	4.93	0.68
9	6.90	0.17

The difference between d-spacing of clays in nanocomposite films (d_{nc}) and that of corresponding pristine clay (d_0) is reported as Δd ($\Delta d = d_{nc} - d_0$) in this table. The effects of each factor on the Δd response are shown in Fig. 1. The hydroxyl groups of the starch could interact directly with the sodium ion of the Na-MMT or with the edge hydroxyl groups of the Na-MMT [21] making a very compatible system. The data show that the largest Δd corresponds to the nanocomposites prepared with modified natural rubber (Fig. 1a). High acting shear forces during melt compounding can cause the diffusion of polymer chains within the silicate galleries, especially for polymers of high molecular weight like the natural rubber [22]. Also, the polar groups of the proteins and lipids, at the surface of natural rubber, may act as a driving force for rubber chains to intercalate into the silicate layers [6]. Although the surface polarities of both clay and natural rubber latex particles are negative [23], the excess of ammonium cations on the surface of stabilized natural rubber latex particles, contribute to match the polarities of the polymer and clay improving their compatibility via electrostatic interactions, which in turn favors intercalation. The layers of the Na-MMT are usually expanded or delaminated by exchanging Na with alkylammonium cations therefore, it can be assumed that the ammonia greatly facilitate the intercalation of the polyisoprene chains [24].

It is observed that the Δd increase with the clay content up to 3 wt.%. A higher loading however has a deterioration effect (Fig. 1b). Indeed, the improvement is usually continued with increasing the clay content up to a percent at which the silicate layers cannot be exfoliated anymore. Afterwards, addition of more amount of clay into the matrix leads to appearance of clay stacks and even aggregates.

The effect of glycerol content on the responses is shown in Fig. 1c. It can be seen that Δd has the highest value when 20% glycerol is used during the nanocomposite preparation. The lower or higher levels of glycerol content do not result in proper gallery spacing. Similar behaviors were found by Chiou et al. [14], who compared the effects of 5, 10, and 15% by weight of glycerol on clay dispersion in extruded starch/clay nanocomposites. In that work, the addition of 5 wt% glycerol has led to an exfoliated structure, whereas with 10% or 15% glycerol the intercalated morphologies have been obtained. When the natural rubber was added in starch/natural rubber/clay nanocomposite samples, Δd was shown to decrease (Fig. 1d).
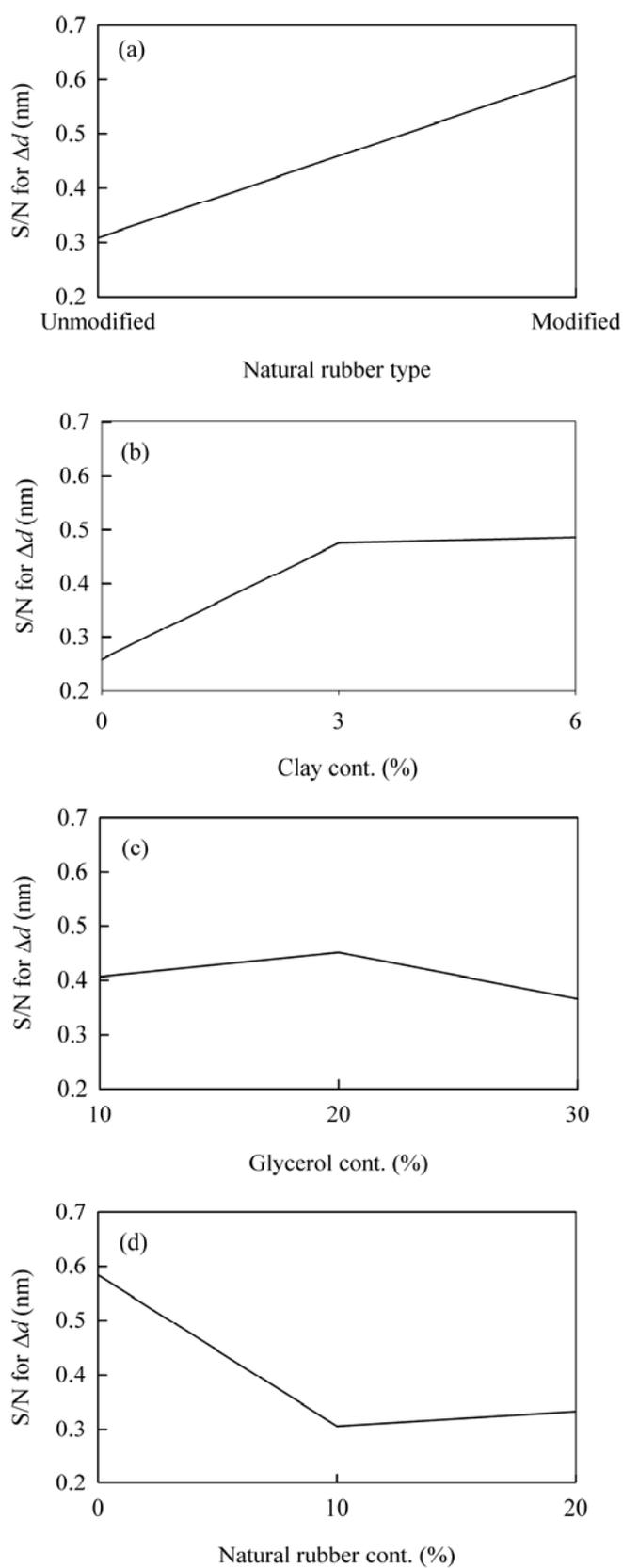
Fig. 1. Effect of factors: a) natural rubber type, b) clay content, c) glycerol content, and d) natural rubber content on Δd of nanocomposite samples.

3.2. Analysis of variance for tensile strength and modulus

The analysis of variance (ANOVA) is a powerful technique in Taguchi method that explores the percent contribution of factors affecting the response. The strategy of ANOVA is to extract the variations that each factor cause relative to the total variation observed in the results [18,25]. The statistical analysis of the results was carried out using Qualitek-4 (Nutek Inc.) software. Table 4 represents the results of tensile strength, modulus and elongation at break in tensile test for all 9 trials. Tables 5 and 6 also show the ANOVA statistical terms for tensile strength and modulus of nanocomposites, respectively.

Table 4: Mechanical properties of samples.

Trial	Tensile strength (MPa)		tensile modulus (MPa)		Elongation at break (%)	
	Replication 1	Replication 2	Replication 1	Replication 2	Replication 1	Replication 2
1	33.3	33.5	1522	1531	14.58	14.64
2	60.2	64.1	4125	4136	3.33	3.37
3	18.6	18.4	946	953	16.11	16.21
4	59.6	59.9	2446	2440	5.31	5.38
5	30.9	40.0	1800	1813	8.41	8.59
6	79.2	79.1	7598	7606	2.49	2.37
7	48.4	48.2	5412	5401	3.00	2.94
8	24.1	24.5	1969	1960	7.12	7.14
9	20.7	20.8	1553	1566	10.30	10.35

The F-ratio in ANOVA tables is a reliable criterion for ranking the factors with respect to their influence. A higher value of the calculated F-ratio for a factor means a greater influence of that factor on the experiment outcome. It is clear from Tables 5 and 6 that the most important contributors to the variability of the results are natural rubber type (A) and clay content (B). The other/error term, in the last row of ANOVA tables, contains thus the information about three sources of variability of the results including uncontrollable factors, factors that are not considered in the experiments, and the experimental error [18]. It should be emphasized that the interpretation of ANOVA table is valid just in the range of considered levels for the factors. That's why the determination of levels is of great importance in any experimental design approach.

Table 5. ANOVA table for tensile strength.

Factors	DOF[a]	Sum of Squares	Variance	F-ratio	Pure Sum	Percent
Natural rubber type	1	83.78	83.78	509.38	83.62	51.55
Clay cont. (%)	2	49.77	24.88	151.29	49.44	30.47
Glycerol cont. (%)	2	16.78	8.39	51.02	16.45	10.14
Natural rubber cont. (%)	2	11.74	5.87	35.68	11.41	7.03
Other/Error	1	0.163	0.163	-	-	0.81
Total	8	162.24	-	-	-	100.00

a. Degree of freedom

Table 6. ANOVA table for modulus.

Factors	DOF	Sum of Squares	Variance	F-ratio	Pure Sum	Percent
Natural rubber type	1	64.82	64.82	2078.0	64.79	62.86
Clay cont. (%)	2	16.21	8.10	259.76	16.14	15.66
Glycerol cont. (%)	2	13.58	6.79	217.68	13.52	13.12
Natural rubber cont. (%)	2	8.43	4.22	135.21	8.37	8.12
Other/Error	1	0.03	0.03	-	-	0.24
Total	8	103.08	-	-	-	100.00

In the following sections the effects of various factors on tensile strength and modulus are comprehensively investigated.

3.3. Effects of factors on tensile properties

The trends in which tensile strength (σ) and modulus (*E*) (in terms of S/N ratio) are influenced when the factors are varied on their levels are shown on main effect plots (Fig. 2). Each point on these plots represents the average of three replicated experimental data on the relevant level.

3.3.1. Effect of natural rubber type

The effect of natural rubber type on tensile strength and modulus of starch/natural rubber/clay samples is observed in Fig. 2a. It is implied that the unmodified natural rubber results in weak improvements in tensile properties compared to that of modified. The significant increase for samples prepared with modified natural rubber could be attributed to the combination of enhanced compatibility between the modified natural rubber and starch and the crosslinking of polyalkenylene chains [7,8,20]. Low elongation of the starch/natural rubber/MMT nanocomposites with unmodified natural rubber could be attributed to partial crosslinking of polyalkenylene chains.

3.3.2. Effect of clay content

Fig. 2b indicates the effect of clay content on tensile properties of the nanocomposite samples. It is observed that the tensile strength and modulus improve with the clay content up to 3 wt.%. A higher loading however has deterioration effect for *E* and σ. In fact, addition of more amount of clay into the matrix leads to appearance of clay stacks that deteriorate the mechanical properties.

3.3.3. Effect of glycerol content

As shown in Fig.2c, the tensile properties for the starch/natural rubber/clay nanocomposites was greater in samples containing 10 wt % of glycerol. It is implied that the sufficient amounts of glycerol plasticize the starch matrix and improves the intercalation process. However, incorporating an extra amount of glycerol into the starch/clay samples inhibits the intercalation of starch/natural rubber into the galleries. This is because the excess amount of glycerol leads to an increase in glycerol–starch interactions that might compete with interactions between glycerol, starch, and the clay surface.

3.3.4. Effect of natural rubber content

The effect of natural rubber content on the responses is shown in Fig. 2d. It can be seen that σ and *E* have the highest value when 10 wt.% natural rubber is used during the nanocomposite preparation. A further increase in rubber contents produces a phase separation in starch/natural rubber blends. These results showed that the addition of rubber to starch–glycerol blends is limited by phase separation [6].
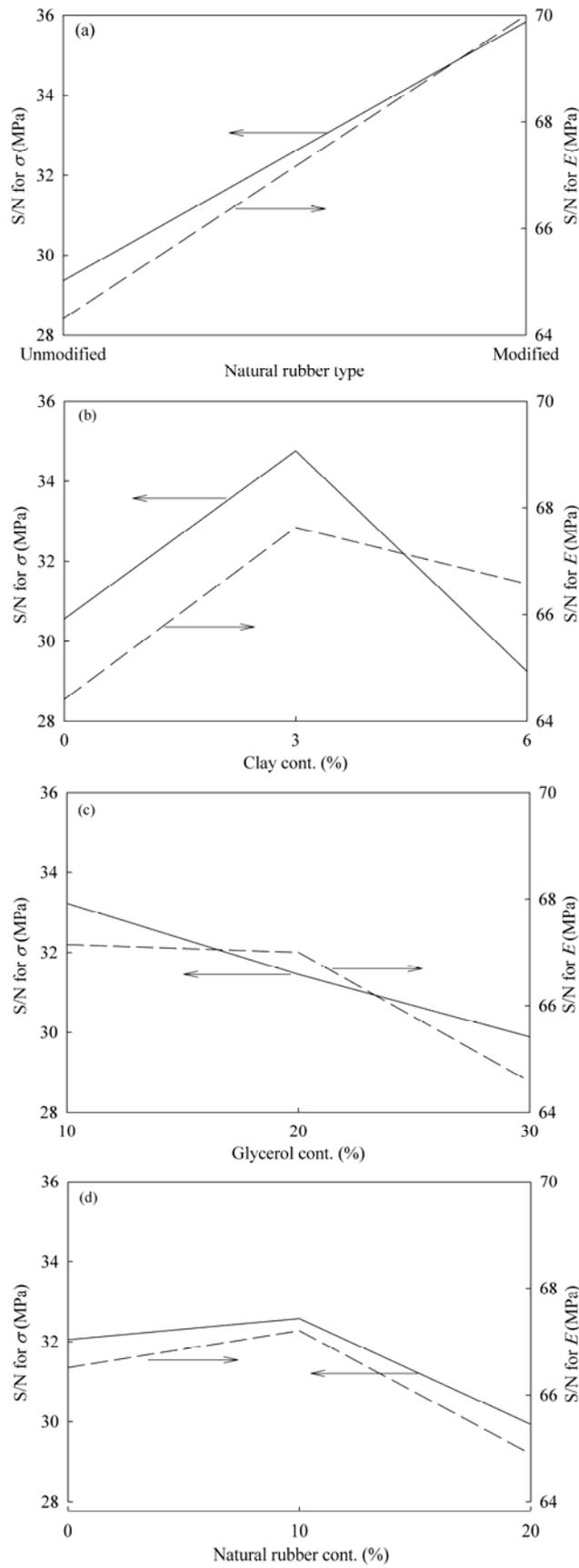
314

Fig. 2. Effect of factors: a) natural rubber type, b) clay content, c) glycerol content, and d) natural rubber content on tensile strength (σ), and modulus (E) of nanocomposite samples.

3.4. Morphology

Fig. 3a shows the SEM micrograph of the fractured surface of the starch/natural rubber/clay nanocomposite (prepared with unmodified natural rubber latex) loading 3 wt.% clay. It reveals that both thermoplastic starch matrix (gray areas) and dispersed rubber phase (white areas) are clearly separated indicating lack of interfacial adhesion. This is expected because natural rubber and thermoplastic starch are immiscible due to the hydrophobic character of the former and the hydrophilic character of the latter [7,8]. Although it has been reported that the proteins and lipids present at the surface of the rubber particles act as compatibilizers between starch and rubber molecules, these interactions are not strong enough to obtain a good dispersion in these blends [6]. On the other hand, the use of modified natural rubber (Fig. 3b) resulted in a finer dispersion and improved interfacial adhesion. It was supposed that the poly(DMAEMA)-grafted polyisoprene chains adhered to the starch phase are responsible for this interfacial adhesion. As reported by other authors, blending of thermoplastic starch with modified polyisoprene leads to the formation of hydrogen bonds between latex particles with a ''hairy layer'' of surface-grafted hydrophilic poly(DMAEMA) and starch molecules [7,26]. The fibrils should have been formed by plastic deformation.
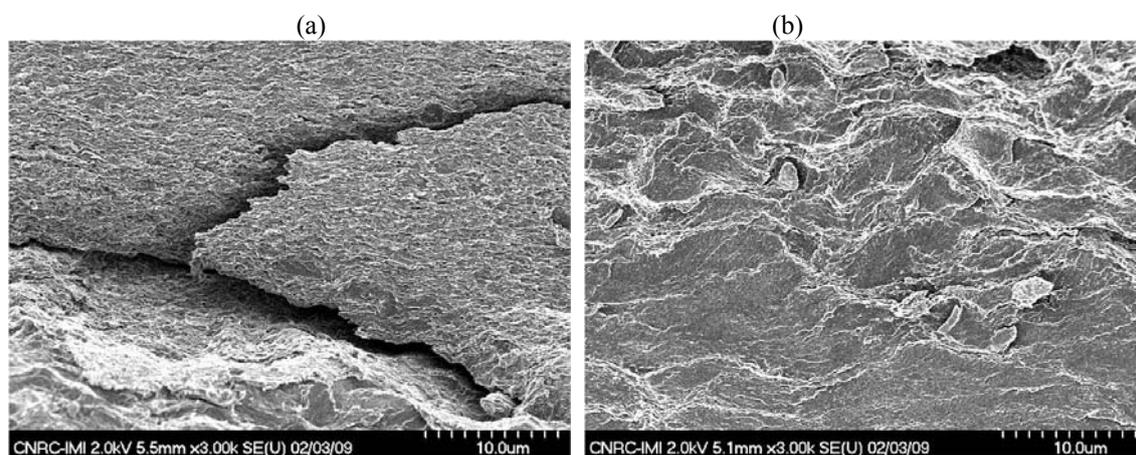

(a)   (b)

Fig. 3. SEM micrographs of starch/natural rubber/clay nanocomposites with a)
unmodified natural rubber, and b) modified natural rubber.

4. Conclusions

Plasticized starch/natural rubber/clay nanocomposites were prepared by melt extrusion technique and the influences of various factors on the morphology and mechanical properties (tensile strength and modulus) of these nanocomposites were statistically analyzed using Taguchi experimental approach. The main conclusions in the range of considered levels can be listed as follows:

- The mechanical properties are strongly influenced by the natural rubber type, the clay content, and the glycerol content, respectively. The natural rubber content was found to be the least significant factor for improvement the mechanical properties in this study.
- The samples prepared with modified natural rubber, represented better mechanical properties in comparison with unmodified natural rubber. Interfacial adhesion of the rubber phase in the thermoplastic starch matrix combined with the natural rubber cross-linking occurring during chemical modification was responsible for this improvement.
- Nanocomposite samples prepared with 3 wt.% MMT represented the best dispersion degree of silicate layers compared to either lower or higher contents.
- The samples prepared with 10% (by weight) of glycerol and natural rubber loading, represented better mechanical properties.

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