

# On the Swelling of Polychloroprene-MMT Nanocomposite Films

Martín Soriano-Luna, Héctor Ismael Núñez-Pérez, Mirna R. Estrada

*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Av. Universidad 3000 UNAM-CU, Distrito Federal 04510, México*

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**ABSTRACT:** For the first time, the effects on the percentage of swelling of fifteen solvents on latex polychloroprene (CR) nanocomposite (NC) films, and typical physical properties were studied. These films were prepared with 2.5, 5.0, 7.5, and 10.0 phr of montmorillonite (MMT) dispersed in water. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) results exhibit both exfoliated and intercalated layers in NC films. It was found that the Young's modulus and hardness increased with the MMT content. Calculations of the crosslink density were used to evaluate the effect of MMT concentration on the percentage of swelling. It was observed that in chloroform CR films showed the maximum swelling and it is therefore the best solvent to calculate the Flory–Huggins polymer–solvent interaction parameter as well as the crosslink density. To find the Flory–Huggins polymer–

solvent interaction parameter, it was preferred to use the Hoftyser and Van Krevelen polychloroprene solubility parameter of 19.2 (MPa)<sup>1/2</sup> (calculated from the molar attraction constants) instead of using the swelling master curve which is not accurate. In all NC films, swelling by organic solvents was reduced by the addition of MMT. The increasing crosslink density with MMT suggests that dispersed clay emulates chemical bonds by hindering solvent migration throughout the polymer matrix and reducing solvent penetration. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2986–2992, 2012

**Key words:** montmorillonite-nanocomposites; polychloroprene films; crosslink density; swelling; solubility parameter; Flory–Huggins polymer–solvent interaction parameter

## INTRODUCTION

Research interest in polymer–clay nanocomposites has seen significant growth over the last two decades.<sup>1</sup> These NC have demonstrated substantial improvement in materials properties (such as mechanical and thermal properties, better flame retardancy, and impermeability) when compared with pristine polymers or conventional micro- and macrocomposite counterparts.<sup>2–6</sup> Because of its high cation exchange capacity, surface area, surface reactivity, and adsorptive properties, montmorillonite (MMT) has been widely used to prepare nanocomposites. The improved gas barrier properties of NCs stem from the increase in the effective diffusion distance caused by the need for the solutes to follow longer paths around the platelets (which have high length/width ratios).<sup>7,8</sup>

To date, research involving layered silicates for the property modification of polymers has been mostly devoted to thermoplastics and thermosetting

resins.<sup>1,2</sup> However, elastomers and rubbers, such as natural rubber (NR),<sup>9</sup> polychloroprene CR,<sup>10–13</sup> polyisoprene (IR),<sup>14</sup> polybutadiene (BR),<sup>15</sup> styrene-butadiene rubber (SBR),<sup>16</sup> and nitrile rubber,<sup>17</sup> are also promising polymeric matrices for the preparation of polymeric NC.<sup>6</sup> MMT polychloroprene nanocomposites have been prepared mainly by melt intercalation<sup>11</sup> and the mechanical stirring of solid CR compounding and roll mill.<sup>18</sup> Because MMT has a high affinity for water,<sup>19</sup> aqueous CR (latex) and aqueous MMT dispersions can also be used to obtain MMT platelet exfoliation.<sup>20</sup>

The study of the degradation and stabilization of polymers is an extremely important area from the scientific and industrial points of view.<sup>21</sup> Remarkably, the majority of the polymer–clay NC research has focused on their preparation techniques, their exfoliated-intercalated structure characterization and the improvement of their mechanical properties, such as the Young's modulus, elongation at break, and maximum tear strength. The main focus of the research on the degradation resistance of CR has been on thermal degradation, UV radiation, biodegradability, and high-energy degradation.<sup>21</sup> Known CR degradation studies include those on thermal degradation,<sup>22</sup> the thermal degradation of partially ozonized CR,<sup>23</sup> degradation by ozone,<sup>24</sup>

Correspondence to: M. R. Estrada (mirna@unam.mx).

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degradation by the photo-Fenton process,<sup>25</sup> and ageing.<sup>26</sup> However, there are no known studies on the swelling of organic solvents on CR NC films. For the most part, only two solvents have been used in elastomers or their clay nanocomposites to determine crosslink density: benzene<sup>27</sup> and toluene.<sup>28</sup> Usually, only one solvent is used at a time. Baah's group has been the only one to work with other compounds, studying such phenomena as mass changes in pristine CR by immersion in acetaldehyde, maleic anhydride, and maleic acid.<sup>29</sup>

In this study, the effects of 15 organic solvents on crosslink density, Young's modulus and hardness of CR MMT nanocomposites are evaluated. These properties were measured before and after swelling, and the changes are reported. Calculations of the crosslink density were used to evaluate the effect of MMT concentration on the percentage of swelling.

## EXPERIMENTAL

### Materials

Polychloroprene latex (*Neopreno 671A*) was purchased from DuPont Performance Elastomers, sodium montmorillonite from Nanocor, organic solvents from Sigma Aldrich (ketone, acetonitrile, benzene, chloroform, diethylamine, *N,N*-dimethylformamide, carbon disulfide, nitrobenzene, tetrahydrofuran, and 1,1,2,2-tetrachloroethane) and from J.T. Baker (ethyl acetate, glacial acetic acid, ethanol, diethyl ether, hexane, and toluene).

### Nanocomposite preparation

MMT-water dispersion was prepared with a 5 wt % of MMT. Water and MMT were mixed at 600 rpm for 24 h with a Caframo mixer. Then polychloroprene latex was added to obtain the final, dried NCs at 2.5, 5.0, 7.5, and 10.0 phr of MMT. After mixing, the films were prepared by casting the mixtures in molds. The films were then dried at room temperature for 24 h. Finally, the films were unmolded and dried at 70°C under vacuum for 3 h. The thickness was kept within  $0.7 \pm 0.05$  mm for all films.

### Nanocomposite characterization

The structure of the dispersed silicate layer in the NCs was studied with XRD and transmission electronic microscopy (TEM). X-ray diffraction patterns of NCs and clay were performed with an X-ray Brucker AXS D8 Advance diffractometer, at room temperature, for 2-theta angles ranging from 2 to 10°. Samples for TEM pictures were encapsulated in resin and cut using an ultramicrotome and glass knives. These samples were examined using a Jeol

transmission electron microscope JEM-1200EX, 120 kV. The Young's modulus and stress-strain curves were determined for a tensile test at 25°C in a DMA Q800 V7.5 Build 127. The samples were cut to  $3.0 \times 0.5$  cm<sup>2</sup>, and tensile tests were performed at a stress rate of 0.1 N/min up to a maximum strength of 18 N. Hardness was determined with a Mitutoyo shore A durometer at 25°C. The crosslink density determination was carried out by swelling the NC film samples in chloroform at 30°C for 1 h.

### Chemical resistance evaluation

The evaluation of the chemical resistance of NC films to organic solvents was determined using the procedures described in the ASTM-D543<sup>30</sup> method, and organic solvents were chosen from the ASTM-F1001<sup>31</sup> method. The samples were cut to  $5.0 \times 2.5$  cm<sup>2</sup>. Three samples were used for each determination, and their mass, width, length, Young's modulus, and hardness were determined before being immersed in the organic solvents. After immersion at 30°C, the mass, length, and width of the samples were immediately measured. The samples were then dried at room conditions for 24 h, under vacuum (380 mm Hg) at 50°C for 3 h. Then mass, length, width, hardness, and Young's modulus were measured again.

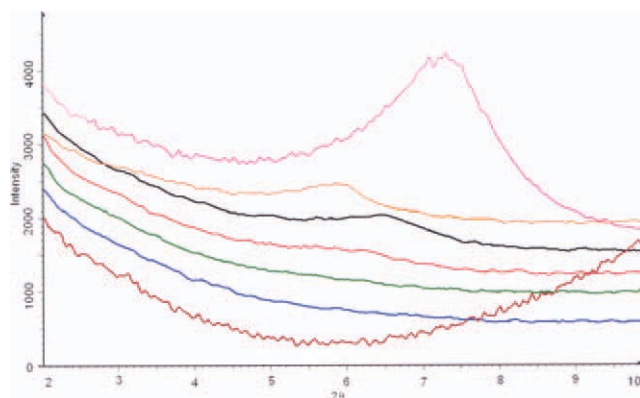
## RESULTS AND DISCUSSION

### X-ray diffraction

Figure 1 shows the X-ray diffractogram of MMT, CR, and their NCs, from bottom to top: MMT-water dispersion (brown), CR (blue), NCs with 2.5 (green), 5.0 (red), 7.5 (black), 10 (orange) phr of MMT, and dry MMT (pink). The characteristic MMT peak is broad and appears at about 7.2° of 2θ (top highest line in Fig. 1). MMT-water dispersion did not present a characteristic interlayer peak ( $d_{001}$ ), thus showing MMT exfoliation; the same is observed at concentration for the 2.5 phr NC. The peak begins to appear slightly at concentration of 5 phr and is more pronounced at 7.5 and 10 phr NCs. The interlayer space of the NCs was slightly increased from 12 Å to 14.2 Å (5.0 phr), 13.3 Å (7.5 phr), and 14.8 Å (10.0 phr). These data suggest that at high concentrations of MMT the clay platelets restack around the CR chains when water evaporates, leading to the formation of intercalated NCs.

### Transmission electronic microscopy

For NC films TEM results exhibit both exfoliated and intercalated layers. Exfoliation was also exhibited in the 5 phr NC (Fig. 2) and the 10 phr NC (Fig. 3).



**Figure 1** X-Ray diffractogram of MMT-water dispersion (brown), CR (blue), nanocomposites (2.5 (green), 5.0 (red), 7.5 (black), 10 (orange) phr), and dry MMT (pink). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

A slight reassembling of the MMT platelets is visible (platelets almost parallel, Fig. 3). At low concentrations, the clay remains exfoliated, but at the two highest concentrations, reassembled sheets are present.

#### Preparation of CR-MMT nanocomposites

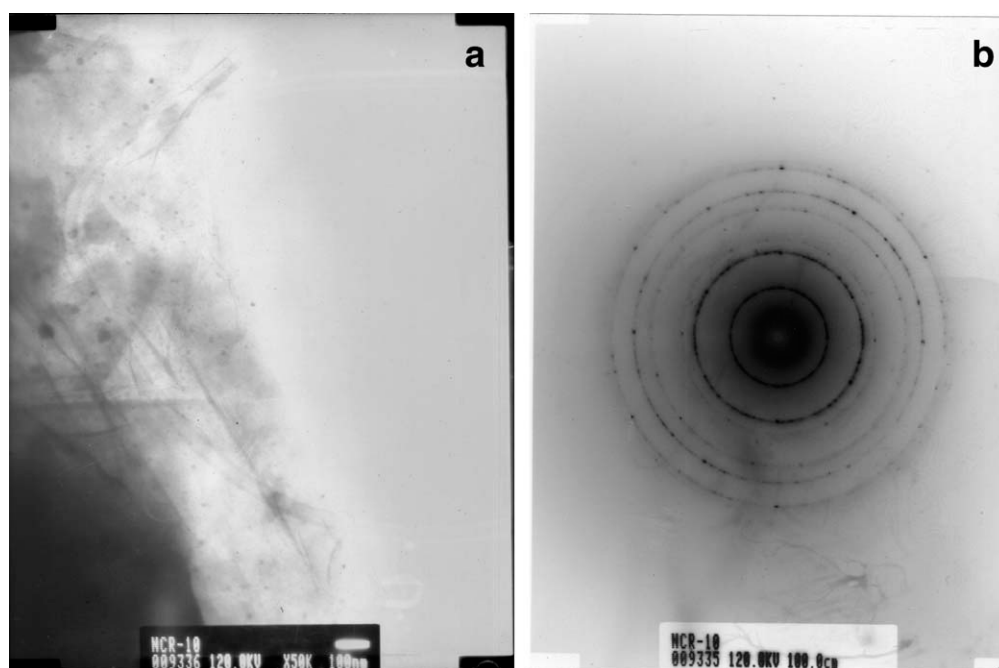
In this work, the obtained NCs were not typically "intercalated," as is usual to observe in thermoplastics NC or *in situ* polymerization, since preparation began with an aqueous dispersion of MMT and was already exfoliated. The preparation of our NCs from a water-MMT suspension and CR latex (Fig. 4) can be described as follows.



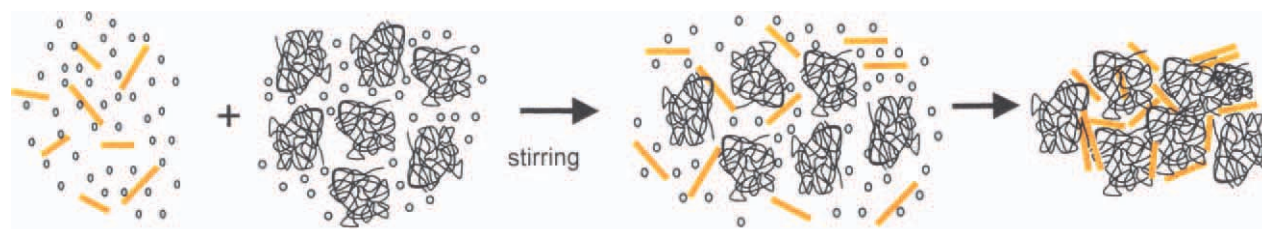
**Figure 2** TEM photograph of the 5 phr NC film.

First [Fig. 4(a)], MMT was dispersed in water by vigorous stirring for 24 h. Exfoliation is supported by the lack of peaks below 10 of  $2\theta$  (corresponding to the interlayer distance  $d_{001}$ ) in the XRD data (see the brown line in Fig. 1).

- CR latex [Fig. 4(b)] was added and mixed by rapidly stirring to produce a homogeneous aqueous dispersion [Fig. 4(c)].
- Then, water was slowly removed to avoid the formation of bubbles in the solid mixture. The majority of platelets remained separated, and



**Figure 3** TEM photograph of the 10 phr NC film and its XRD pattern.



**Figure 4** Preparation of CR-MMT nanocomposites. (a) exfoliated MMT in water, (b) CR latex, (c) CR and MMT-water dispersion, (d) dried CR-MMT nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

those in close proximity to one another were able to reassemble, in particular when MMT concentration is high. In some cases, CR chains avoided reassembling, which led to a NC that was a mixture of exfoliated, intercalated and reassembled MMT platelets in the dried film [Fig. 4(d)].

#### Determination of the crosslink density of polychloroprene by swelling

To evaluate the effect of MMT concentration on the percentage of swelling, crosslink density calculations were carried out.

The crosslink density ( $v_x$ ) was determined with swelling measurements (in chloroform at 30°C) and by applying the Flory–Rehner equation<sup>32,33</sup>:

$$v_x = -\frac{\ln(1 - \phi_2) + \phi_2 + \chi_1 \phi_2^2}{\phi_1 \left( \phi_2^{1/3} - \frac{\phi_2}{2} \right)}, \quad (1)$$

where  $\phi_2$  is the volume fraction of the polymer in the swollen mass,  $\phi_1$  is the molar volume of chloroform, and  $\chi_1$  is the Flory–Huggins polymer–solvent

interaction term. The volume fraction of polymer ( $\phi_2$ ) was calculated by the expression

$$\phi_2 = \frac{\frac{W_p}{\rho_p}}{\frac{W_p}{\rho_p} + \frac{W_s}{\rho_s}}, \quad (2)$$

where  $W_p$  is the dry mass of the polymer sample,  $\rho_p$  is the dry polymer density,  $W_s$  is the solvent mass in the swollen sample, and  $\rho_s$  is the solvent density. The Flory–Huggins polymer–solvent interaction parameter can be calculated from the Hildebrand–Scatchard and Flory theories using

$$\chi_1 = \chi_H + \chi_S \quad (3)$$

The component  $\chi_H$  is related to the heat of mixing of the polymer with the solvent, and it is found that<sup>34</sup>:

$$\chi_H = \frac{\phi_1}{RT} (\delta_1 - \delta_2)^2. \quad (4)$$

The entropic component is  $\chi_S$  and is approximately equal to the reciprocal of the lattice coordination number.<sup>34</sup> It has been reported that it has a value between 0.3 and 0.5, but the value of 0.34 is adopted for all the systems, as Blanks and Prausnitz

**TABLE I**  
Solvent Solubility Parameters and Percentage of Swelling of CR NC in Several Solvents

Solvents	Solubility parameter $\delta_1$ (Mpa <sup>1/2</sup> )	Swelling at various MMT Concentrations (%)			
		0 pcr	2.5 pcr	5 pcr	10 pcr
Hexane	14.9	17	16.5	14.4	10
Diethylether	15.1	92	74.2	72.3	58.9
Diethylamine	16.4	167	131.4	110.4	70.7
Toluene	18.2	577	535.5	530.8	431
Tetrahydrofuran	18.6	635	596.8	570	405.2
Benzene	18.8	690	482.1	410	387.5
Chloroform	19.0	1096	1029.8	948.2	582.9
Acetone	20.3	39	38.6	38.08	33.69
Carbon disulfide	20.5	866	608	609.9	410.5
Nitrobenzene	20.5	517	287.5	303.1	199.5
Acetic acid	20.7	27	15.1	16.2	13
Acetonitrile	24.3	6	4.5	4.3	3.5
Dimethylformamide	24.8	70	60.6	54.4	43

TABLE II  
Volume Fraction, Crosslink Density, and Young's Modulus of CR NC

Sample	Volume fraction $\phi_2$	Molar volume $\phi_1(\text{m}^3/\text{mol})$	Interaction parameter $\chi_1$	Crosslink density $\nu \chi$ ( $\text{mol}/\text{m}^3$ )	Young's modulus (MPa)
CR	0.099	$8.11 \times 10^{-5}$	0.342	56.09	1.18
CR-2.5 MMT	0.104	$8.11 \times 10^{-5}$	0.342	62.72	2.53
CR-5.0 MMT	0.111	$8.11 \times 10^{-5}$	0.342	70.27	6.96
CR-7.5 MMT	0.140	$8.11 \times 10^{-5}$	0.342	112.41	9.00
CR-10 MMT	0.175	$8.11 \times 10^{-5}$	0.342	180.26	16.55

find a mean value of 0.34.<sup>35–37</sup> This leads to the equation

$$\chi_1 = \frac{\phi_1}{RT} (\delta_1 - \delta_2)^2 + 0.34, \quad (5)$$

where  $\phi_1$  is the molar volume of solvent at the normal boiling point ( $\frac{\text{cm}^3}{\text{mol}}$ ),  $R$  is the ideal gas constant in ( $\frac{\text{cm}^3 \text{MPa}}{\text{molK}}$ ),  $T$  is the absolute temperature (K), and  $\delta_1$  and  $\delta_2$  are the Hildebrand solubility parameters of the solvent and polymer, respectively, in  $(\text{MPa})^{1/2}$ . To find which solvent can be used to crosslink determination, the percent of swelling ( $W_s/W_p \times 100$ ) each of the NCs was obtained. In Table I, it can be observed that chloroform is the solvent that swells the most at all concentrations of MMT. As chloroform showed the highest degree of swelling, its solubility parameter value ( $\delta_1 = 19(\text{MPa})^{1/2}$ ) was used to calculate the Flory–Huggins polymer–solvent interaction term and the crosslink density.

The solvent affinity with MMT could be classified into three types, according to the increase in the weight percent produced by solvent penetration: high-affinity (>500%), medium-affinity (between 150% and 70%) and low-affinity (<70%). Solvents with solubility parameters closer to that of CR produced the highest swellings. That means that chloroform presents the closest affinity to CR NC.

The solubility parameter is related with the heat of vaporization ( $\Delta H_{\text{vap}}$ ) as follows:

$$\delta_1 = [(\Delta H_{\text{vap}} - RT)/\phi_1]^{1/2}$$

As polymers cannot be evaporated, indirect methods have to be used for the determination of their solubility parameters. Hoftyzer and Van Krevelen (H+vK) have calculated for polychloroprene a solubility parameter value of  $\delta_2 = 19.2 (\text{MPa})^{1/2}$  from the molar attraction constants.<sup>38</sup> This value is close to that which was obtained with chloroform, the best solvent found for our samples. The criterion for complete solvent–polymer miscibility is that  $\chi_1 < 0.5$ .<sup>39</sup> As a result, the difference in solubility parameters of solvent and polymer must be small. Other reported experimental values fall between 16.8 and 18.9  $(\text{MPa})^{1/2}$ .<sup>34,38</sup> With a chloroform

solubility parameter value of  $\delta_1 = 19(\text{MPa})^{1/2}$ , and, using H+vK data  $\delta_2 = 19.2 (\text{MPa})^{1/2}$  for CR, we can obtain the Flory–Huggins polymer–solvent interaction parameter  $\chi_1$  and the crosslink density ( $\nu \chi$ ).

$$\chi_1 = \frac{8.12 \frac{\text{cm}^3}{\text{mol}}}{8.314 \frac{\text{cm}^3 \text{MPa}}{\text{mol}} * 303.15 \text{K}} [(19 - 19.2)(\text{MPa})^{1/2}]^2 + 0.34 = 0.342$$

This value is close to  $\chi_1 = 0.31$  which was reported for CR in benzene with  $\delta_{\text{C}_6\text{H}_6} = 18.8(\text{MPa})^{1/2}$ .<sup>40</sup> Table II contains the values of volume fraction, molar volume, interaction parameter, crosslink density, and the Young's modulus found for CR and all concentrations of CR NC.

Results show that crosslink density values increase with the MMT content in the NCs. In fact, no chemical crosslinkages were produced by the MMT, but the effects of the well-known "tortuous path"<sup>41</sup> produced by the well-dispersed nanometric plates emulate crosslinking. This leads to a physical effect that reduces the penetration of solvent molecules in the polymer matrix and increases the crosslink density obtained from the calculation made using the Flory–Rehner equation.

The Young's modulus of the CR and its four NCs are presented in Table II. The correlation of the

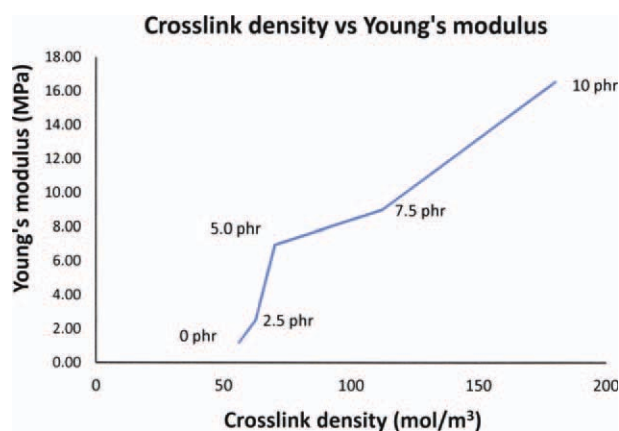
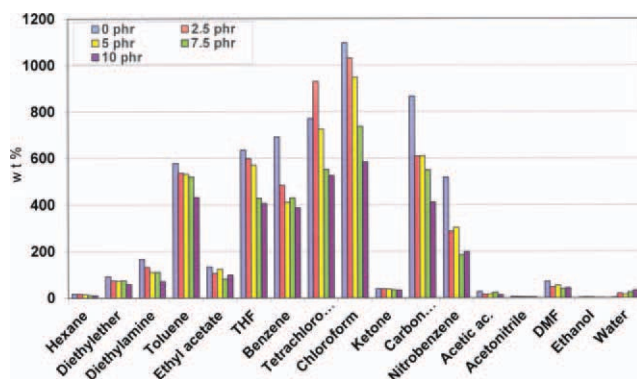


Figure 5 Crosslink density vs. Young's modulus for CR and nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



**Figure 6** Changes in the weight percent of swollen samples in different solvents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Young's modulus with the crosslink density is shown in Figure 5. The addition of MMT leads to an increase in the Young's modulus due to a higher crosslink density value.

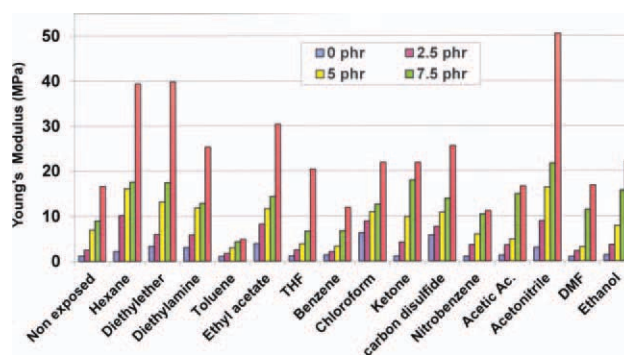
### Effect of organic solvents

The effects of organic solvents on weight, length, width, shore hardness, and Young's modulus were evaluated using the ASTM-D543 method.

Figure 6 indicates that the addition of MMT leads to a decrease of swelling in the NCs with respect to pristine CR for all organic solvents and that swelling was the lowest for the sample with 10 phr of MMT.

Swelling in NCs with 10 phr of MMT was up to 50% lower compared to pristine CR swelling in chloroform, benzene, nitrobenzene, carbon disulfide, diethylamine, acetic acid, and diethyl ether. The ketone swelling was reduced the least (by 13%) in comparison to pristine CR swelling.

Swelling in the NCs with 10 phr of MMT was reduced by up to 61% in high-affinity solvents (nitrobenzene), 58% in medium-affinity solvents (diethyl-



**Figure 8** Changes in the Young modulus of samples which were dried after immersion. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

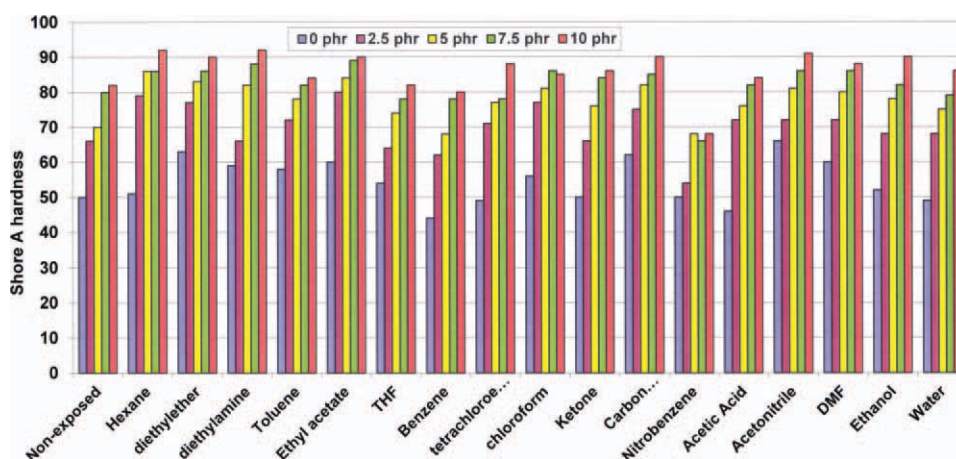
amine), and 52% in low-affinity (acetic acid) solvents. These results indicate that the swelling decrease caused by the addition of MMT can be independent of the affinity of the solvent to pristine CR.

The addition of MMT to pristine CR leads to an increased hardness that is dependent on the concentration of MMT in the NCs. Figure 7 indicates that in the majority of the cases, the hardness of NCs after drying remained similar to that of those samples not undergoing immersion in solvents.

Changes in the Young's modulus (Fig. 8) showed a similar behavior to that of the hardness property. Almost all solvents caused an increase in the Young's modulus. High-affinity solvents reduced the Young's modulus. This can be result of the residual presence of these solvents within the samples. In the majority of the cases the Young's modulus values increase with the MMT content in the NCs.

### CONCLUSIONS

CR-MMT film NCs were prepared at 2.5, 5.0, 7.5, and 10.0 phr and were exfoliated at low concentrations and with reassembled MMT plates around the



**Figure 7** Changes in the hardness for samples which were dried after immersion. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

CR chains in the case of the two highest concentrations. From the percent of swelling from all the NCs in several solvents, we observed that chloroform showed the maximum swelling and is therefore the best solvent to calculate the Flory–Huggins polymer–solvent interaction parameter as well as the crosslink density. The addition of MMT to CR increased the crosslinking density values, which led to a remarkable decrease in swelling in organic solvents and to an increase in the Young's modulus of CR NC films.

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## References

- Hussain, F.; Hojjati, M.; Okamoto, M.; Gorga, R. E. *J Compos Mater* 2006, 40, 1511.
- Sinha-Ray, S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
- Schadler, L. S.; Brinson, L. C.; Sawyer, W. G. *JOM-US* 2007, 59, 53.
- Alexandre, M.; Dubois, P. *Mater Sci Eng* 2000, 28, 1.
- Caseri, W. R. *Mater Sci Tech-Lond* 2006, 22, 807.
- Sengupta, R.; Chakraborty, S.; Bandyopadhyay, S.; Dasgupta, S.; Mukhopadhyay, R.; Auddy, K.; Deuri, A. S. *Polym Eng Sci* 2007, 47, 1956.
- Zhong, Y.; Janes, D.; Zheng, Y.; Hetzer, M.; De Kee, D. *Polym Eng Sci* 2007, 47, 1101.
- Rhim, J. W.; Ng, P. K. W. *Crit Rev Food Sci* 2007, 47, 411.
- Maiti, M.; Bhattacharya, M.; Bhowmick, A. K. *Rubber Chem Technol* 2008, 81, 384.
- Yeh, M. H.; Hwang, W. S.; Cheng, L. R. *Appl Surf Sci* 2007, 253, 4777.
- Kim, Y.; White, J. L. *J Appl Polym Sci* 2003, 90, 1581.
- Yeh, M. H.; Hwang, W. S. *Mater Trans* 2006, 47, 2753.
- Caffarena, V. D.; Capitanleo, J. L.; Ogasawara, T.; Pinho, M. S. *Mater Res-Ibero-Am J* 2008, 11, 335.
- Ding, Y. F.; Pawlus, S.; Sokolov, A. P.; Douglas, J. F.; Karim, A.; Soles, C. L. *Macromolecules* 2009, 42, 3201.
- Kooshki, M. M.; Arani, A. J. *E-Polymers* 2009, Article Number: 132.
- Meneghetti, P.; Shaikh, S.; Qutubuddin, S.; Nazarenko, S. *Rubber Chem Technol* 2008, 81, 821.
- Wang, Q. G.; Zhang, X. H.; Qiao, J. L. *Chinese Sci Bull* 2009, 54, 877.
- Yeh, M. H.; Hwang, W. S.; Chang, Y. C. *Jpn J Appl Phys* 1, 2005, 44, 6847.
- Belarbi, H.; Haouzi, A.; Douillard, J. M.; Giuntini, J. C.; Henne, F. *J Colloid Interf Sci* 2007, 308, 216.
- Karger-Kocsis, J.; Wu, C. M. *Polym Eng Sci* 2004, 44, 1083.
- Pandey, J. K.; Reddy, K. R.; Kumar, A. P.; Singh, R. P. *Polym Degrad Stabil* 2005, 88, 234.
- Budregeac, P.; Seagal, E. J. *Therm Anal* 1998, 53, 441.
- Anachkov, M. P.; Rakovski, S. K.; Stoyanov, A. K. *J Appl Polym Sci* 1996, 61, 585.
- Ivan, G.; Giurginca, M. *Polym Degrad Stabil* 1998, 62, 441.
- Freitas, A. R.; Rubira, A. F.; Muniz, E. C. *Polym Degrad Stabil* 2008, 93, 601.
- Kalidaha, A. K.; De, P. P.; Sen, A.K. *Polym Degrad Stabil* 1993, 39, 179.
- Amin, M.; Nasr, G. M.; Attia, G.; Gomaa, A. S. *Mater Lett* 1996, 28, 207.
- Varghese, S.; Karger-Kocsis, J. *Polymer* 2003, 44, 4921.
- Baah, C. A.; Baah, J. I. *Mater Des* 2001, 22, 403.
- ASTM-D543–87.
- ASTM-F1001–99a.
- Cambridge Polymer Group Inc. *CPGAN # 005*. Available at: [http://www.campoly.com/application\\_notes.html](http://www.campoly.com/application_notes.html).
- Flory, P. J. *J Chem Phys* 1950, 18, 108.
- Sheehan, C. J.; Bisio, A. L. *Rubber Chem Technol* 1966, 39, 149.
- Blanks, R. F.; Prausnitz, J. M. *Ind Eng Chem Fundamentals* 1964, 3, 1.
- Zhu, L.; Wool, R. P. *Polymer* 2006, 47, 8106.
- Ovejero, G.; Pérez, P.; Romero, M. D.; Guzmán, I.; Díez, E. *Eur Polym J* 2007, 43, 1444.
- Van Krevelen, D. W.; Te Nijenhuis K.; *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*, 4th ed., Elsevier: Amsterdam, The Netherlands, 2009; p 189.
- Barton, A. F. M. *Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*; CRC Press Inc: EU, 1990; p 5.
- Kawasaki, N.; Hashimoto, T. *J Polym Sci Pol Chem* 1973, 11, 671.
- Neilson, L. E. *J Macromol Sci Chem A1* 1967, 929.