Rigid Poly(vinyl chloride)/ Halloysite Nanocomposites

M. Mondragón^{*}, Y.S. Roblero-Linares^{**}, M.E. Sánchez -Espíndola^{***} and B.E. Zendejas-Leal^{****}

*ESIME-IPN Unidad Azcapotzalco, Av de la Granjas 682, Col Sta. Catarina, 02550 México, D.F., mmondragon@ipn.mx
**ESIQUIE-IPN, México, D.F., yojan_23@hotmail.com
*****ENCB-IPN, México, D.F., sanz@gmail.com
*****CINVESTAV Departamento de Física, México, D.F., blanca@fis.cinvestav.mx

ABSTRACT

Polyvinyl chloride (PVC)/ halloysite nanotubes (HNT) nanocomposites were prepared by melt blending of PVC and HNT using a two-roller mill. The microstructure and mechanical properties were investigated. Both Izod impact and tensile strength of nanocomposites filled with HNT were similar to those of unfilled PVC. However, PVC stiffness was reduced due to the addition of HNT and elongation was prominently improved at 3 and 5 wt. % HNT content. Elongation improvement was attributed to both fibrillation induction of the PVC matrix by HNT and HNT orientation, as indicated by the results of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The decrease in stiffness seemed to be an interesting side effect.

Keywords: Poly (vinyl chloride), nanotubes, mechanical properties, morphology.

1 INTRODUCTION

Rigid poly (vinyl chloride) (PVC) is increasingly used in building industry to replace wood and metal in windows, pipes, sheets, and other profiles [1]. Within recent years, inorganic fillers have been utilized to elaborate PVC nanocomposites and enhance not only toughness of PVC matrix, but also its tensile strength, electric properties and heat resistance [2].

These nano-fillers, with diameters in the range of several nanometers, include calcium carbonate, silica and montmorillonite (MMT). Small amounts of these particles had lead to significant improvement in the properties of the nanocomposites [3]. A mineral that has not yet been used widely in the plastic industry are the halloysite nanotubes (HNT). They are multiwalled kaolinite nanotubes, containing octahedrally coordinated Al³⁺ and tetrahedrally coordinated Si⁴⁺ in a 1:1 stoichiometric ratio. HNT are readily obtainable and are much cheaper than carbon nanotubes (CNTs). Besides, the complicated control on the exfoliation and intercalation needed for layered clay such as montmorillonite it is not necessary for the nanotubes [4].

In the current study, an attempt is made to prepare and characterize PVC/HNT nanocomposites.

2 EXPERIMENTAL METHODS

A master dry blend containing 100 parts PVC resin (K 57), 1.5 parts stabilizer, 10 parts impact modifier, 1.8 parts processing aid, 0.8 parts internal lubricant, and 0.3 parts external lubricant was prepared. The PVC masterbatch powders were hand blended with 1, 3, 5 and 8 wt. % of HNTTM (obtained from NaturalNano, Inc) and melt-mixed using a two-roller mill at 180° C for 15 min. These nanocomposites were compression-molded at 170° C for 3 min to give 1 and 3 mm thick plates. The samples for characterization of morphology and mechanical tests were cut from these plates.

Tensile tests were performed with 1-mm-thick specimens at a crosshead speed of 2 in/min on a 4301 Instron testing machine according to ASTM D638. Notched impact test were performed with 3-mm-thick specimens according to ASTM 256, the pendulum weight was 1.020 lb. The specimens after tensile test were subsequently examined in a JSM-5800LV scanning electron microscope (SEM). The fracture surfaces were coated with a thin layer of gold before SEM observations. The morphologies of compressed specimens were examined with a JEM 1010 transmission electron microscope (TEM) at an accelerating voltage of 60 kV.

3 RESULTS AND DISCUSSIONS

3.1 Mechanical properties

Figure 1 shows the Izod impact and tensile strength of the PVC/HNT nanocomposites. Tensile strength stayed on a nearly constant level at filler content up to 8 wt. %. Mechanical properties of polymer composites are strongly influenced by interfacial adhesion between polymer matrix and filler [5]. Tensile strength behavior suggested that stresses were inefficiently transferred to the HNT due to poor filler matrix-interactions.

Impact strength was not favorably affected by changes in HNT concentration. High aspect ratio fillers are able to induce large stress concentrations near their edges, reducing the absorbed impact energy of polymer composites [6]. HNT agglomerates could have also affected unfavorably the impact strength.



Figure 1: Izod impact a) and tensile strength b) of nanocomposites *vs.* HNT content.

Figure 2 shows the Young's modulus and elongation at break of the PVC/HNT nanocomposites. It was observed that stiffness was reduced due to the addition of HNT. Usually this property is increased in the composites as a result of the high modulus of the particulate fillers. However, other workers have reported that treated fillers tend to decrease the stiffness of some polymeric nanocomposites due to a relatively compliant layer at the interface [7].

The elongation increased by the addition of HNT showing a maximum at 3% HNT concentration, from which it decreased. Similar elongation behavior has been reported for polymers filled with other nanofillers, specifically montmorillonite type clays, due to platelet orientation and chain slippage [1]. Considering that the stiffness of the PVC/HNT nanocomposites decreased compared to pristine PVC matrix, the increase in the elongation seemed to be a combined effect of both interfacial viscoelastic deformation and HNT orientation.

3.2 Morphology

Figure 3 shows the TEM micrographs of the PVC/HNT nanocomposites loading 3 and 5 wt. % HNT. It can be



Figure 2: Young's modulus a) and elongation b) of nanocomposites *vs.* HNT content.



Figure 3: TEM micrographs of PVC/HNT (3 and 5 wt %) nanocomposites.

observed individual and aggregated nanotubes dispersed inhomogeneously in the PVC matrix, although a clear orientation is observed.

Figure 4 shows the SEM micrograph of the tensilefractured surface of the PVC/HNT nanocomposite containing 5% HNT. A clear plastic fibrillation was shown, similar morphologies has been reported for fractured surfaces of other polymer nanocomposites [8]. The elongation at break of this nanocomposite is 60%, a value much higher than of the PVC matrix. Therefore, HNT can be acting as a toughening agent not only because of their orientation, but also because they can induce fibrillation of the PVC matrix.



Figure 4: SEM micrographs (x500) of the tensile-fractured surface of PVC/ 5 wt % HNT nancocomposite.

4 CONCLUSIONS

The effect of HNT on the mechanical properties and morphology of PVC/HNT nanocomposites were investigated. Izod impact and tensile strength of the nanocomposites were not improved compared to unfilled PVC. On the other hand, incorporation of HNT improved the elongation at break and reduced the Young's modulus, which could be attributed to interfacial viscoelastic deformation, HNT orientation and induction of fibrillation of the PVC matrix by HNT, as corroborated by SEM and TEM micrographs.

The authors appreciate the finance support from the Project APOY-COMPL-2008 No. 90219 supplied by CONACYT and the Project No. 20091006 supplied the SIP-IPN.

REFERENCES

- M. Tian, G. Chen and S. Guo, Macromol. Mater. Eng. 290, 927, 2005.
- [2] S. Sun, C. Li, L. Zhang, H.L. Du and J.S. Burnell-Gray, Eur. Polym. J. 42, 1643, 2006.

- [3] A. Kalendova, M.Pospisil, L. Kovarova, D.Merinka, M. Valaskova, H. Vlkova, J. Dimonik and P. Capkova, Plast. Rubb. Compos. 33, 279, 2004.
- [4] B. Guo, Y. Lei, F. Chen, X. Liu, M. Du and D. Jia . Appl. Surf. Sci. 49, 2715, 2008.
- [5] A.P. Mathew, K. Oksman and M. Sain, J. Appl. Polym. Sci. 97, 2014, 2005
- [6] F. Haupert and B. Wetzel. In "Polymer Composites from Nano-to Macro-Scale", K.Friedrich, S. Fakirov and Z. Zhang, Eds., Springer, 45-62, 2005.
- [7] M.Q.Zhang, M.Z. Rong and K. Friedrich. In "Polymer Composites from Nano-to Macro-Scale", K.Friedrich, S. Fakirov and Z. Zhang, Eds., Springer, 25-44, 2005.
- [8] S. Xie, S. Zhang, B. Zhao, H. Qin, F. Wang and M. Yang, Polym. Int. 54, 1673, 2005.