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Preparation and characterization of a magneto-polymeric nanocomposite: Fe_3O_4 nanoparticles in a grafted, cross-linked and plasticized poly(vinyl chloride) matrix

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Abstract

In this work two kind of materials: (1) grafted, cross-linked and plasticized poly(vinyl chloride) (PVC) ‘‘plastic films’’ and (2) magnetic plastic films ‘‘magneto-polymeric nanocomposites’’ were prepared. Precursor solutions or ‘‘plastisols’’ used to obtain the plastic films were obtained by mixing PVC (emulsion grade) as polymeric matrix, di(2-ethylhexyl)phthalate (DOP) as plasticizer, a thermal stabilizer based in Ca/Zn salts, and a cross-linking agent, 3-mercaptopropyltrimethoxysilane (MTMS) or 3-aminopropyltriethoxysilane (ATES), at several concentrations. Flexible films were obtained from the plastisols using static casting. The stress–strain behavior and the gel content (determined by Soxhlet extraction with boiling THF) of the flexible films were measured in order to evaluate the effect of the cross-linking agent and their content on the degree of cross-linking. The magneto-polymeric nanocomposites were obtained by mixing the optimum composition of the plastisols (analyzed previously) with magnetite (Fe_3O_4)-based ferrofluid and DOP. Later, flexible films were obtained by static casting of the plastisol/ferrofluid systems. The magnetic films were characterized by the above-mentioned techniques and X-ray diffraction, vibrating sample magnetometry and thermogravimetrical analysis.

Keywords: Magneto-polymeric; Nanocomposites; Magnetite; PVC

1. Introduction

The synthesis and characterization of new and novel materials with optimized properties, called ‘‘composite materials’’, are the objective of the advanced materials research. An appropriate approach in this way is to develop composite materials combining the properties of individual systems, such as magnetic nanoparticles and polymer matrixes. The study of magnetic nanoparticles has attracted much interest from both points of view: fundamental, due to the interesting mechanisms, which produce that phenomena, and applied, due to the wide variety of possible applications [1,2]. On the other hand, poly(vinyl chloride) (PVC) is a polymer which has a lot of characteristics suitable for industrial applications such as: good mechanical properties, good resistance to acidic and basic environments, fire retardancy, good processability and, in addition, it offers the advantage of low cost [3].

In our particular case, we are interested in combining the magnetic properties arising from the magnetite nanoparticles (contained in a ferrofluid) and the mechanical properties provided by the polymer matrix of grafted, cross-linked and plasticized PVC, which can be used to obtain magnetic plastic films for a wide variety of possible technological applications [4]. The use of cross-linking agents allow us, throughout the permanent network formation, to control the visco–elastic properties of the polymeric matrix and therefore to have formulations for different applications.

2. Experimental procedure

The chemical reagents used in this work were: emulsion PVC (Vinycel 124) K value 69 supplied by Polycid, di(2-ethylhexyl)phthalate (DOP), Ca/Zn salts (NT-223) from

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Chemical Additives of México, 3-mercaptopropyltrimethoxysilane (MTMS), 3-aminopropyltriethoxysilane (ATES), tetrahydrofuran, iron (III) chloride hexahydrate, iron (II) chloride tetrahydrate, ammonium hydroxide and oleic acid supplied by Aldrich.

The formulations used to obtain the plastic films, based in parts per hundred of PVC (phr), were: PVC 100, DOP 140, Ca/Zn 4, and different amounts of cross-linking agent (MTMS or ATES) 2, 4, 6 and 8 phr, these samples were cross-linked at room temperature. The samples with 8 phr were immersed in hot water (80 °C) during 4 h. The ferrofluid (14% weight of Fe_3O_4) was synthesized following a procedure reported previously [5]. The formulations used to obtain the magneto-polymeric nanocomposite were: PVC 100, DOP 140, Ca/Zn 4, ATES 8 and different amounts of ferrofluid 5, 10, 20, 30, 40, 50 phr. The DOP content was always adjusted to have 140 phr. The formulations (for plastisols and plastisol/ferrofluid systems) were mechanically mixed at room temperature for 90 min. Flexible films were obtained then using static casting and curing them at 185 °C for 5.5 min.

To evaluate the effect of the cross-linking agent content: (1) on the mechanical properties, the stress–strain behavior of the films were measured at 80 °C, in accordance with ASTM D-412-98a, using a SFM-100KN United Testing S and (2) on the cross-linking degree, the gel contents were determined by Soxhlet extraction for 24 h with boiling tetrahydrofuran. The effect of the ferrofluid on the plastic films was evaluated using the mentioned techniques and X-ray diffraction (XRD), vibrating sample magnetometry and thermogravimetrical analysis.

3. Results and discussion

The stress–strain behavior represented as the ultimate tensile strength (UTS) and elongation at break (% *E*) for plastic films cross-linked at room temperature with different cross-linking agent contents is showed in Fig. 1. It can be seen that UTS and % *E* of samples with MTMS increase slightly as the cross-linking agent content increase. The UTS increase from 586 to 861 kPa and % *E* increase from 282% to 418%. In this way, the samples with ATES show a similar behavior, that is to say, there are not big differences between each one of UTS and % *E* values. The UTS values range was from 827 to 1316 kPa and the % *E* values range was from 350% to 420%. Moreover, the measurements of gel content, which are shown in Table 1, do not show important differences with respect to cross-linking agent content, taking in to account the error of that technique. The cross-linking in hot water of the samples with 8 phr led to gel content values of 14% and 45% for samples with MTMS and ATES, respectively. The effect of the cross-linking agent on the mechanical properties (UTS and % *E*) and on the gel content of samples with MTMS, cross-linked at room temperature and in hot water, suggests that in these samples is occurring degradation of the PVC chains, due to, probably, a poor reactivity of thiol group in the cross-linking agent [6]. However, the samples with ATES show a higher cross-linking with the cross-linking agent content increase, as it is indicated by the UTS and % *E* results and, especially, when the cross-linking occur in hot water, such behavior is expected for PVC matrix [7].

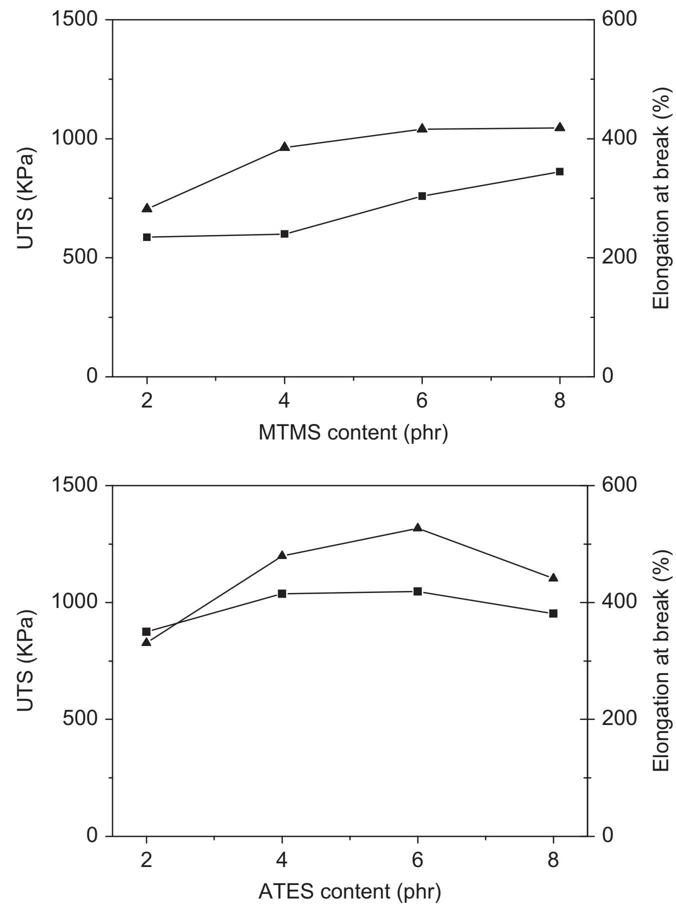

Fig. 1. Ultimate tensile strength (▲) and elongation at break (■) for plastic films with different amounts of MTMS (upper) and ATES (lower) measured at 80 °C.

Table 1
Gel content of plastic films with different amounts of MTMS and ATES cross-linked at room temperature

Cross-linking agent (phr)	Gel content (%)	
	MTMS	ATES
2	28.82	12.22
4	25.68	14.80
6	26.48	14.18
8	27.24	22.32

Fig. 2 shows the XRD patterns of: (1) Fe_3O_4 (JCPDS 19-0629), (2) ferrofluid and (3) a magneto-polymeric nanocomposite with 50 phr of ferrofluid. The spectrum of the ferrofluid shows a clear correspondence with the reported pattern of magnetite while the spectrum of the nanocomposite shows only the main peak. This can be