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NEW Ti-LNR (LIQUID NATURAL RUBBER HYBRID MATERIAL PREPARED BY SOL-GEL METHOD: PREPARATION, STRUCTURE AND PROPERTY BEHAVIOUR

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Abstract- New organic-inorganic composites (OIC) have been prepared by sol-gel process from metal alkoxides such as $Ti[O(CH_2)_3CH_3]_4$ with liquid natural rubber (LNR). *In situ* polymerization of $Ti[O(CH_2)_3CH_3]_4$ in the matrices of liquid natural rubber(LNR) has been successful in producing lightly colored, new transparent flexible materials. The materials obtained showed good macroscopic and microscopic homogeneity. Studies also indicate that the range of molecular weight of the LNR is also very important in obtaining good film material. The amount of Ti alkoxide added into the natural rubber polymer very much influences the structure and morphorlogy of the materials. Dynamic mechanical spectroscopy, scanning electron microscopy and stress strain experiments were utilized to investigate the properties of the composites. Other analytical techniques including FTIR, TGA and DSC were also been used to provide more information of the microscopic and macroscopic composition and physical properties in the OIC materials. Some of the composite of Ti-LNR obtained showed better tensile strength values and good optical transparency.

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Introduction

The use of sol-gel techniques for the preparations of Organic-Inorganic-Composites (OICs)[3-10] has been widely used in the recent years[1-16]. Similar hybrid materials of inorganic alkoxides and organic polymer are also known as ORMOSILs[1], CERAMERS[2]. Sol-gel technique is basically based on a two step reaction, i.e. hydrolysis and condensation of liquid soluble inorganic alkoxides. Much of the work carried out has been to develop materials used as coatings, membranes, electronic and optic materials and tough materials. Much of these works were carried out using various commercially available polymers such as modified poly(tetramethylene oxide) - (PTMO), poly(dimethylsiloxane) - (PDMS), poly(methylmetacrylate) - (PMMA) with various silica alkoxides as the inorganic component. Other metal alkoxides such as titanium tetraisoproxides and zirconium isopropoxides were also employed[5,13-17].

Here we report the successful preparation of IOCs using *insitu* polymerization of titanium alkoxides in LNR. LNR has terminal hydroxyls which will provides the possibility of forming secondary bonds between LNR and the inorganic network, thus increasing the compatibility between the components involved. The presence of such functionalities will provide possible sites for the secondary interactions between the LNR matrix and the titania network following the hydrolysis and condensation reactions. Titanium n-butyl alkoxide has been used due to its higher reactivity towards hydrolysis and condensation compared to silicon alkoxides[18,19].

The preliminary results of physical and mechanical properties of this composites characterized using various techniques such as dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), infrared spectroscopy (FTIR), tensile and UV is presented.

Sample Preparations

A series of OIC film samples with varying amount of tetrabutyl ortho-titanate[Ti(O-nBu)$_4$] in a 5 wt% LNR in toulene solution was prepared via the following procedures. No catalyst was used in the preparation, while the amount of water used is the inherent quantity present in isopropanol. Table 1 and Table 2 shows the list of LNR-titania sample composition.

A 5 wt% LNR solution was prepared in toluene. Then, known amounts of Ti(O-nBu)$_4$ in 30 mL 2-propanol was added dropwise into the polymer solution under vigorous stirring. The mixture was continously stirred and heated in an oil bath with the temperature of between 60 °C and 80 °C for at least 24 hr. until a homogeneous solution was obtained. The sol-gel reaction i.e. hydrolysis, condensation and cross linking was initiated. The whole preparation was carried out in nitrogen atmosphere with N_2 flow during the first 24 hr. of stirring. The nitrogen flow was essential during the mixing in view of the high relative humidity content (~80%) in our laboratory. Homogeneous, transparent with light yellow to dark golden colored films were obtained with the thickness of 0.3 to 0.6 mm.

Results and Discussion

The present simpler sol-gel technique employed in this study has yielded homogenous, transparent and fairly strong OIC films using liquid natural rubber as the matrix phase and titanium butoxide as the disperse phase. This technique has successfully converted the LNR which is originally a viscous liquid to a solid phase. Table 1 shows the series of OICs prepared in this study.

Table 1- List of LNR-titania sample composition prepared

Wt. of LNR used (g) in 100 mL toulene	Wt. of [Ti(O-Bu^n)$_4$] used (g)	Wt% of TiO_2 by TGA
3.55	0.65	2.9
3.55	1.21	6.6
3.55	1.07	6.9
3.55	2.10	12.5
3.55	4.03	18.8
3.55	5.13	26.5

The weight % of Ti(O-nBu)$_4$ used during the preparations ranges from 15% to almost 60%. However, during the discussion that follows the wt% of titania refers to the final titania content which has been determined using TGA (Figure 1) technique as weight percent residue above 700 °C. This point must be emphasied because not all of titania alkoxide used are involved in the sol-gel process. Increasing the amount of titania in OICs has changed the appearance of the OICs film in two ways. Firstly, the film has been transformed from being rubbery to rigid and hard film. Above 25 wt% of titania, the film became brittle. Secondly, the colour of the film changes from light yellow to dark gold as the loading increases.

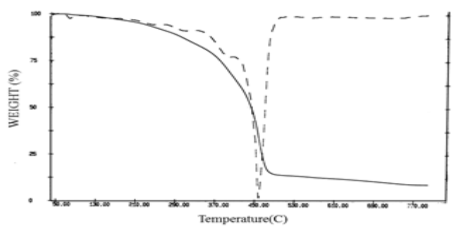

Fig. 1- Sample TGA thermogram of LNR-Ti composite prepared (12.5 wt% titania)

The decomposition temperature of the polymeric component ranges from 400 °C to 450 °C. This value shows very little variation with the contents of titania in the composites. This suggests weak intermolecular interactions between formed titania-LNR network and some microscopic phase separations. The thermogram pattern however showed some interesting features similar to those observed in other titania composites[5]. The TGA thermograms indicate that the water and alcohols (i.e. isopropanol and n-butanol) were released at ~220 °C and ~340 °C respectively. In comparison, TGA thermogram for titania prepared using a similar sol-gel process without the organic matrix shows a single decomposition peak at 120 °C. The higher temperature for the release of water and alcohol implies that water and the alcohol molecules are more strongly associated to the inorganic network rather than the LNR network. There also a possibility of the alcohol molecules been trapped within the interpenetrating network form as is evident from the peak found in ~ 400 °C region.

As expected the results demonstrate a clear trend of increasing modulus with increased contents of titania, while the reverse was observed for the elongation properties of the samples. Similar trends have been observed in other titania containing hybrid materials[5,14]. The enhancement in the modulus of the OICs especially those at higher titania content i.e. about 20% is rather unexpected. The results seem to indicate that the level of the interaction in the crosslinking and other network formation between LNR and titania is not to create a strong and stiff OICs.

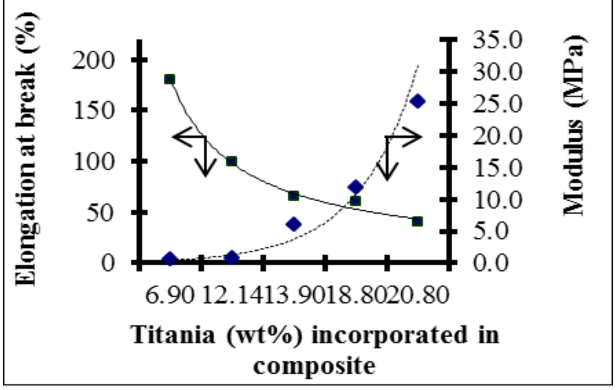

Fig. 2- Amount of titania incorporated in composite vs. elongation and modulus

Increasing the titania content from 7 to 21 wt% has resulted in the reduction of the elongation at break from 180 to 40% respectively. This implies that the incorporation of titania into LNR matrix has given rise to a relatively hard and brittle composites. The presence of titania inhibit the mobility and flexibility of the rubber molecules in a stress-strain plot showing the effect of titania loading on the tensile properties of IOCs. The tensile strength of 8 MPa for 21 wt% titania-LNR shows in Figure 2, film clearly indicates that the composite possesses rather poor strength properties.

UV-VIS spectra for the films obtained showed little variation of the wavelength(nm) as a function of the amount of titania contents in the composite. The composites film absorbs below 350 nm. However, the percentage transmittance(%T) of the film is directly related to the titania content, i.e. increasing amount of titania result in higher %T. Composite film with 13 and 20 wt% titania content show 20 and 80 %T respectively. Further investigations are been carried out.

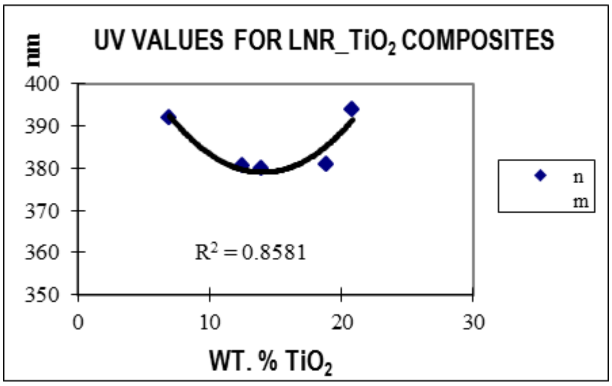

Fig. 3- Wavelength of initial absorption by composites vs amount of titania in composites

FTIR spectrum shown in Figure 4 suggests that the olefinic bonds of the polyisoprene unit in LNR were preserved in the composites in absorption peaks at 1662 and 880 cm-1. Strong broad band at ca. 3500 cm-1, characteristic of the Ti-OH are found in all of the samples

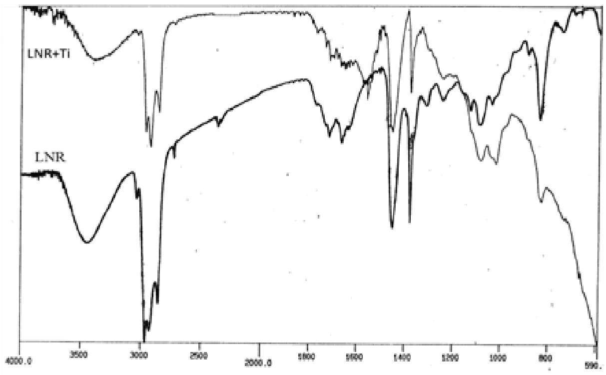

Fig. 4- FTIR spectrum of LNR and LNR-Ti composite

No effort to correlate the peak area to the titania contents were made. In addition, weak absorption bands at 1570 and 500 cm-1 are characteristic of Ti-O. The IR spectrum also indicate that tetrahedral titanium oxide is not at all present, since peaks at 960 cm-1 were absent in any of the spectrum[5].

Conclusions

An easy route to prepare transparent organic-inorganic composites (OICs) from LNR or titanium butoxide has been presented. This work has demonstrated that natural organic polymer, i.e. LNR can be modified by the formation of highly cross-linked inorganic networks via *in situ* polymerization of titanium alkoxides. A transparent composite with higher Tg values and well-dispersed titania throughout the matrix was obtained. This preliminary study has also provided some useful insight into the interaction between organic polymers and inorganic network formed by sol-gel technique. Further work with other inorganic metal alkoxides as well as other natural rubber derivatives are currently been carried out in our laboratory.

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