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Development of PVC/Silica Hybrids Using PVC Plastisols

Marianne Gilbert,[*1] *Siavash Haghighat,*[2] *Soo Keow Chua,*[3] *Soo Yeng Ng*[4]

Summary: A novel method for producing a plasticised PVC with increased porosity has been developed, by the use of an organic-inorganic hybrid. Silica was produced in situ from tetraethoxysilane via a hydrolytic sol-gel processing route. Tetrahydrofuran was used as co-solvent, and γ-glycidyloxypropyl-trimethoxysilane as coupling agent. The films produced were transparent, with moderate mechanical properties. A film containing 20% silica showed a 45% increase in water vapour permeability.

Keywords: in-situ formation; poly(vinyl chloride)(PVC); silicas; sol-gel; water permeability

Introduction

A major disadvantage of plasticised poly-(vinyl chloride) (PVC-P) when used as a leather replacement in garments and upholstery is its low permeability.

This paper investigates the scope for producing organic-inorganic hybrids by incorporating tetraethoxysilane (TEOS) into a PVC plastisol, and then carrying out a sol-gel reaction involving hydrolysis and condensation of the TEOS to produce a fine dispersion of silica in situ. The permeability characteristics of the films produced are examined. The in situ hydrolysis and condensation process has been shown [1] to be capable of producing a three dimensional crosslinked titania network homogeneously distributed in PVC. The nature of the network is controlled by solvent, pH and temperature. In PVC based battery applications, it has found that porosity can be increased by silica [2,3], while flexible PVC/silica composites produced by a plastisol/plastigel technology have been found to have enhanced permeability to water vapour [4]. Ogoshi and Chujo investigated the effect of solvent on hybrid production using tetramethoxysilane and PVC [5].

Experimental

The PVC plastisol formulation used is shown in Table 1. Tetraethoxysilane (TEOS) was used as the precursor for SiO_2 production while γ-glycidyloxypropyl-trimethoxy-silane (GOTMS) was used as a coupling agent. In this initial work the coupling agent was not optimised, but GOTMS which had been found to be successful with other polar polymers [6,7], was selected. GOTMS was added to TEOS, followed by THF, water, and an acid catalyst. The alkoxysilane precursor composition is given in Table 2. The alkoxysilane precursor was prehydrolysed in-situ with the PVC-P precursor by mechanical mixing to form a low viscosity transparent sol. Miscible solutions were produced. By varying the amount of alkoxysilane precursor in the mix a range of sols were produced with silica concentrations ranging from 0–20% by weight.

Initially films were cast by spreading on to a Melinex sheet using a K bar; subsequently a Mathis Laboratory Coating device was used, enabling more uniform films to be produced. Films were vacuum dried to remove air, then heated to fuse the

[1,2] IPTME, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK
Fax: (+44) (0)1509 223949
E-mail: M.Gilbert@lboro.ac.uk
[3] Precision Polymer Engineering, Greenbank Road, Blackburn BB1 3EA, UK
[4] Singapore, niko_@yahoo.com

Table 1.
Plastisol Formulation

Paste PVC	EVIPOL MP7154	EVC	100
Plasticiser	DIDP	Exxon	100
Heat stabiliser	Ca/Zn Interlite ZP9005	Akcros	4
Solvent	Tetrahydrofuran (THF)	Fisher Chemicals	10

Table 2.
Alkoxysilane Precursor (based on 100g of TEOS)

Material	Function	Weight g
TEOS Tetraethoxysilane	Silica source	100.0
GOTMS γ-glycidyoxypropyltrimethoxy-silane	Coupling agent	13.5
Tetrahydrofuran (THF)	Solvent	143.0
Water		8.0
Hydrochloric acid, HCl	Acid Catalyst	2.9

PVC and simultaneously carry out the sol-gel reaction. The silica/PVC-P hybrids were expected to undergo controlled phase-separation during gelation, producing a co-continuous morphology in the network. The process used is summarised in Figure 1.

The morphology of the hybrid films was examined using optical microscopy, Pulsed Force Mode Atomic Force Microscopy (AFM) and Field Emission Gun Scanning Electron Microscopy (FEGSEM). Topography, adhesion variation and stiffness differences across the samples were monitored. Tensile properties of the films were measured, and water vapour permeability was measured at 21 °C using a gravimetric method in which the films were used to seal weighed jars containing desiccant.

Results and Discussion

Silica/PVC-P hybrid films were transparent. Both tensile strength and elongation were reduced by the incorporation of silica, as shown in Fig. 2, but reductions in these values were only about 10%, and did not depend on silica concentration. As little change in properties was observed even in the presence of 20% silica, it appeared that the GOTMS compatibilser was effective in linking the silica particles and matrix. Water vapour permeability increased as

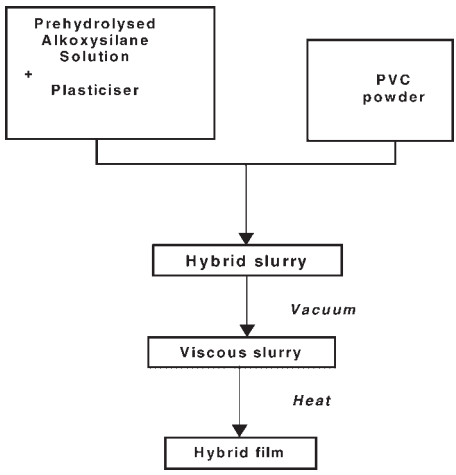

Figure 1.
Schematic representation of hybrid preparation.

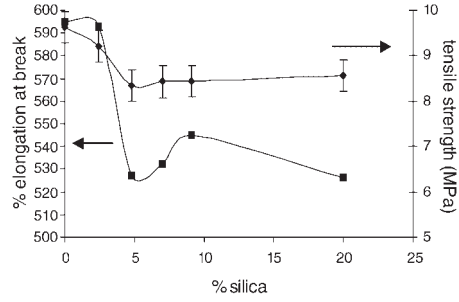

Figure 2.
Tensile properties of hybrid films.

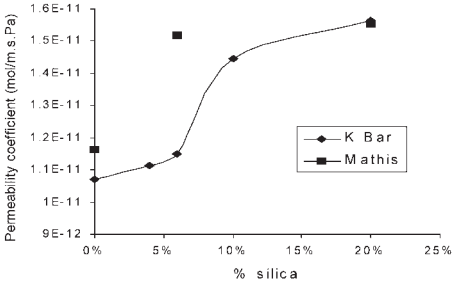

Figure 3.
Moisture permeability of hybrid films.

shown in Fig. 3, although not as much as observed previously [4].

Structures observed by AFM for samples containing 0% and 20% silica are shown in Fig. 4. In the adhesion photographs, Fig. 4(b), brighter areas correspond to higher adhesion to the probe, i.e. the polymer phase, while in Fig. 4(c), which shows sample stiffness, brighter regions equate to those that are harder, leading to the conclusion that a discrete phase consisting of silica has been produced, according to equations shown in Scheme 1.

Further morphological information was obtained using FEGSEM with an energy dispersive X-ray analysis (EDAX) attachment. The micrograph and associated X-ray spectrum for plasticised PVC without silica are shown in Fig. 5.

As expected the structure of the film is uniform and rather featureless, while X-ray analysis shows the presence of chlorine, carbon and oxygen. Similar results for films containing 6% and 20% silica are shown in Fig. 6a and 6b respectively. These figures clearly show that spherical silica particles, of the order of 2–3μm in diameter, have been produced.

However, the examination of a larger area by optical microscopy showed that some much bigger particles were also

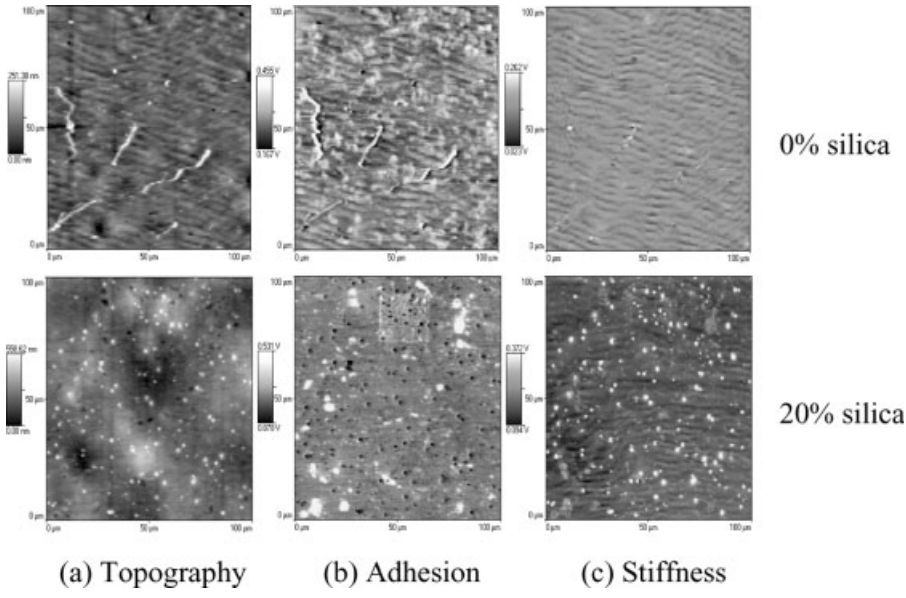

Figure 4.
AFM images.

$$Si(OCH_2CH_3)_4 + 4\,H_2O \rightarrow Si(OH)_4 + 4\,CH_2CH_3OH$$
$$Si(OH)_4 \rightarrow SiO_2 + 2\,H_2O$$

Scheme 1.
Hydrolysis and condensation reactions.

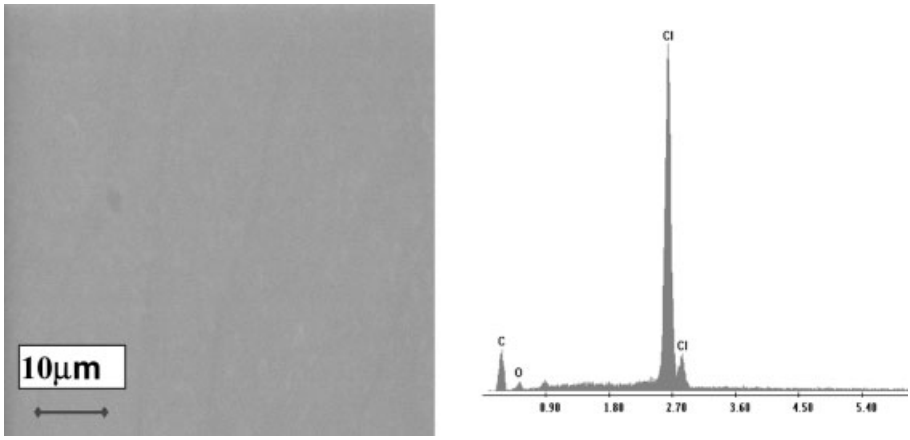

Figure 5.
FEGSEM micrograph and X-ray spectrum for plasticised PVC.

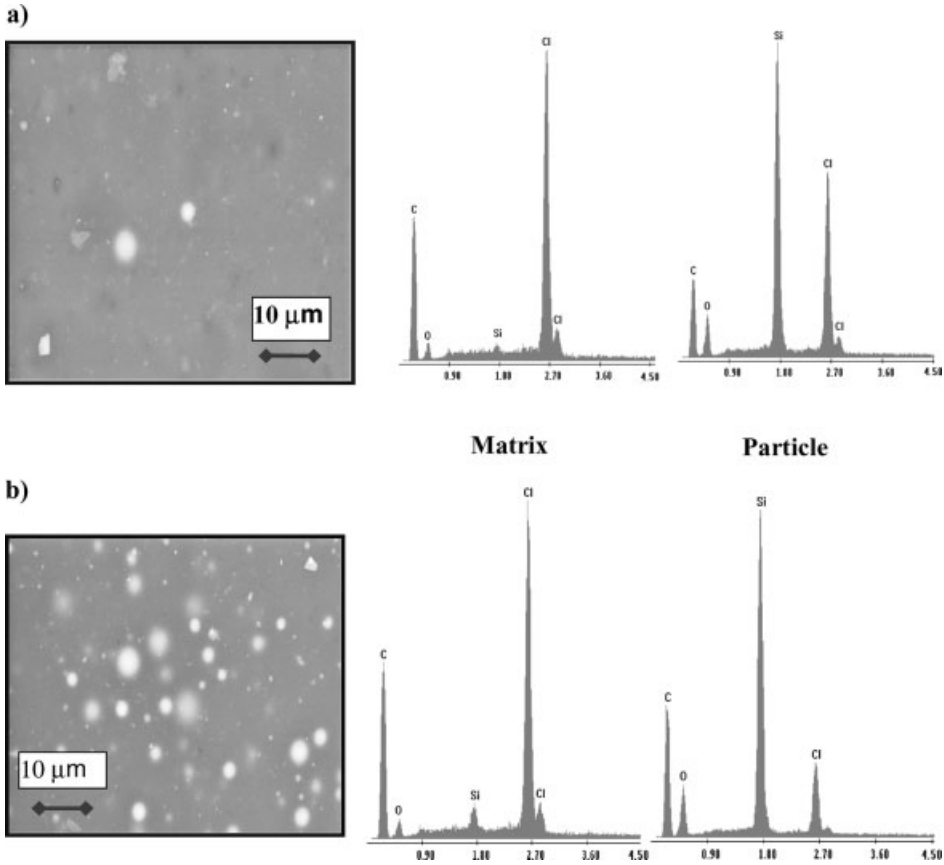

Figure 6.
(**a**) Plasticised PVC film containing 6% silica. (**b**) Plasticised PVC film containing 20% silica.

present – particles up to 30 μm in diameter were detected, whilst the average size was about 5 μm. These large sizes explain why the sample appears transparent – the large particles cause very low angle scattering, and the scattered intensity is low. (The low angle scattering also causes some reduction in film clarity). The discrete structures which have been produced, rather than the anticipated network structure, probably account for the lower than anticipated moisture permeability.

An ATR spectrum of a plasticised PVC was subtracted from that of the film containing 20% silica was consistent with SiO_2.

Conclusions

A novel method for producing a plasticised PVC with increased porosity has been developed, by the use of an organic-inorganic hybrid. The films produced were transparent, with and mechanical properties were adequate, substantially unchanged from the plasticised PVC film without silica. A film containing 20% silica showed a 45% increase in water vapour permeability. Further work is required to develop a network structure rather than discrete silica particles, by modifying conditions used, in order to increase further the moisture permeability.

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