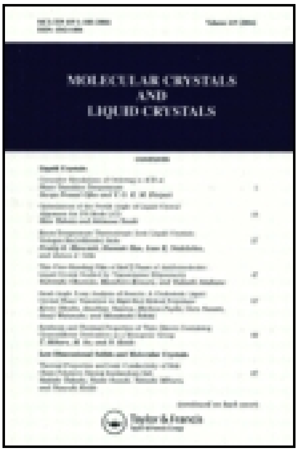

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# EFFECT OF CROSSLINKING SULPHOCHLORINATED POLYETHYLENE WITH POLYVINYL CHLORIDE

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Abstract
In this paper, the effect of ammonia solution as a crosslinking agent for sulphochlorinated polyethylene (SCPE) before and after being blended with polyvinyl chloride (PVC) is examined, by means of swelling measurement determinations. It is seen that the higher the concentration of $NH_3$ used, the higher the percentage of undissolved SCPE in the sample. Moreover the present results prove that an appreciable degree of crosslinking in the blend requires the employment of extreme conditions such as the use of fractionated SCPE and immersion of the blend sample for long periods in the curing media.

## INTRODUCTION

Interpenetrating polymer networks have in recent years become a prominent member of the family of polymer alloys. IPNs have been prepared in the form of 100% solids and in solution, starting with either the respective monomers or prepolymers together with their respective crosslinking agents, catalysts and/or initiators. Crosslinking appears to be one of the most important ways for increasing the miscibility between the components of the network, being also expected that by crosslinking one of the components, changes in its overall behaviour must occur.

In spite of polyvinyl chloride (PVC) capability of being miscible with a great number of polymers, its morphology is not yet fully understood and its complex semicrystalline structure has been found to persist even in polymer blends which are ostensibly miscible. Sulphochlorinated polyethylenes (SCPEs) at 30% chlorine content do not contain crystalline regions because the chlorine atoms are randomly distributed and make the structure less regular. Besides, the $SO_2Cl$ groups enable the SCPE to be crosslinked. The main interest of this paper is to see how ammonia solutions affect the miscibility behaviour of SCPE before and after being blended with PVC.

## EXPERIMENTAL

## Materials

A sulphochlorinated polyethylene with 43% Cl content and 1% S as $SO_2Cl$ groups, was provided under the name of Hypalon 48 by Du Pont U.K. Ltd. Before using it, it was necessary to remove the talc added to it by the manufacturers. This was performed by preparing a 5% solution of SCPE in methyl ethyl ketone (MEK) analar grade (BDH Chemicals Ltd). The MEK was previously dried over a molecular sieve. The resultant solution was centrifuged at 14,000 rpm for 30 min at 17°C (the ultracentrifuge used was an MSE high speed 25). The supernatant liquid was poured into a petri dish. The MEK was then allowed to evaporate slowly by partially covering the petri dish until a film was obtained. Last traces of MEK were eliminated by leaving the film a minimum of 7 days in a vacuum oven at 50°C. Du Pont specifies that this material is sulphochlorinated by a solution process which should yield in principle an amorphous material. However, when viewed between cross polars in a microscope (Nikon Optiphot Universal), characteristic spherulitic structures were still present.

To prepare SCPE with 50% Cl and 1% S as $SO_2Cl$ groups, the chlorosulphonation method followed was based on McQueen's[1] method. This procedure, is an extension of the chlorosulphonation reaction of small molecules known as the Reed reaction[2,3]:

$$RH + Cl_2 + SO_2 \xrightarrow{h\nu} RSO_2Cl$$

This reaction follows a free radical substitution mechanism and needs visible or u.v. light to catalyse the homolysis of $Cl_2$[2].

In the present work, 60g of high density polyethylene (HDPE) (BDH Chemicals Ltd.) were placed with 1.2 litres of chlorobenzene analar grade (BDH Chemicals Ltd.) in a 2 litre round bottom flask fitted with a glass stirrer, a reflux condenser and inlets for $N_2$, $Cl_2$ and $SO_2$. Lecture bottles containing $Cl_2$ and $SO_2$, were connected to wash bottles with concentrated $H_2SO_4$ which in turn were connected to flowmeters and then to gas inlets. A soda lime trap was used to collect unreacted $Cl_2$ and $SO_2$. $N_2$ was bubbled slowly into the chlorobenzene which was warmed up to 130°C to dissolve the HDPE. Stirring was provided continuously during the whole reaction. When the HDPE was completely dissolved, two tungsten lamps (60 watts each) were turned on and $Cl_2$ was passed into the flask with a flow of 40 ml/min for 110 min. The temperature was then allowed to drop to 56°C and, while keeping $Cl_2$ constantly flowing, the $SO_2$ was passed into the flask for 53 min. Then the introduction of $SO_2$ was stopped and the temperature was increased again, letting the $Cl_2$ flow for another 6.25 h. To determine the content of Cl and S already introduced to the HDPE, elemental analysis was carried on. For this purpose, a few ml of the product were precipitated and washed with an excess of methanol. This was left drying at 50°C for a week. The sample was analyzed in an elemental analyzer (Carlo Erba, model 1102) which provided facilities for the determination of C, H, O, and N. Cyclohexanone-2,4-dinitro-phenylhydrazone and benzoic acid were used as standards for the CHN and O analysis respectively. The S content was calculated by assuming that all the S and O were present in $SO_2Cl$ groups; the Cl content was then obtained by difference. At this stage the sample contained 45.55% of $Cl_2$ and 0.63% of S.

As the Cl and S contents were still below the required level, the rest of the product kept in solution was chlorosulphonated again. On this occasion, the $Cl_2$ was introduced for 3.20 h and the $SO_2$ for 55 min. The final product, whose Cl and S content were determined as before, had ≈50% Cl and 1.0% S, which was a suitable composition for the purposes of this work.

A bulk polymerized PVC known as Breon M 110/50 (BP Chemicals Ltd.), was purified by centrifuging a 5% solution in dried MEK at 14,000 rpm for 30 min. The supernatant liquid was cast on a petri dish, allowing the solvent to evaporate slowly. Traces of MEK in the resultant film were eliminated by leaving the sample for one week at 48°C in a vacuum oven.

## Blend preparation

SCPE/PVC blends with 40 (B40) and 50% w/w (B50) of SCPE were prepared by solvent casting. The method followed will be explained here.

An approximate total of two grams of both polymers (weighed in the required proportions) were mixed for 24 hours in a common solvent to yield a 5% W/V solution. The resultant solution was poured into a petri dish. The solvent was allowed to evaporate slowly by covering the petri dish until a film was obtained. Depending on the volume of the solvent used, the total evaporation took about 4 days. To remove traces of solvent left in the film, the petri dish was left at 50°C for one week. In order to control the thickness of the film (≈ 0.5 mm) the initial weighing of the polymers was based on the approximate density of the blend (average of the densities of both components) and the diameter of the petri dish used. The solvent used for casting was tetrahydrofuran (THF) (BDH, analar).

## Crosslinking reactions

It is believed that $NH_3$ crosslinks the SCPE by the formation of polysulphonamide crosslinks[3]. The probable mechanism of crosslinking may consist of firstly an $S_N2$ reaction of the $SO_2Cl$ groups with the $NH_3$, to yield a sulphonamide, and secondly an $S_N2$ reaction between the sulphonamide and a $SO_2Cl$ in another chain forming the crosslink.

In the present work, SCPE was crosslinked with ammonia solution [Sg 0.88 (35% $NH_3$), BDH Chemicals Ltd.]. Ammonia gas was not employed because its use would require more sophisticated equipment. Sections of the solvent cast SCPE measuring 40x40 mm, were crosslinked by immersing them in different concentrations of ammonia solution (5.0, 20.0, 30.0 and 35% $NH_3$) at room temperature for one week.

The progress of reaction was followed by measuring the weight percentage remaining undissolved after solvent extraction with MEK (technical grade, BDH Chemicals Ltd. ). It was found that although the percentage of undissolved material increased proportionally to the concentration of $NH_3$, the values were low (≈ 20%) even with the most concentrated solution. The experiments were repeated with fractionated SCPE using the fraction of highest molecular weight (the fractionation was performed at room temperature by precipitating the SCPE with methanol from a 1% w/v solution of the polymer in benzene) giving a higher conversion under the same previous croasslinking conditions. Further experiments were repeated under more extreme conditions.

SCPE when blended with PVC was also crosslinked by the ammonia solutions using the technique described for crosslinking SCPE before blending.

## Swelling measurements

The procedure used to calculate the degree of crosslinking by swelling measurements is based on the method of Ellis and Welding[4]. The specimen, a rectangular section obtained from the cured polymer or blend, was firstly accurately weighed (average weights 0.2g) and then placed in a stoppered bottle containing 50 ml of the swelling liquid MEK, which was a good solvent for the polymer or polymer components of the blend. The weight of the immersed sample was then checked periodically during seven days. To avoid drifts in weight in the swollen sample, caused by solvent evaporation, the following weighing procedure was used: after removing the sample from the solvent, the excess was removed by quickly shaking the sample which was then immediately dropped into a stoppered tared bottle. This was then weighed and the sample returned immediately to the swelling solvent.

## RESULTS AND DISCUSSION

Fig. 1 shows the weight percentage of undissolved cured polymer when SCPE/PVC 40/60 (B40) and 50/50 (B50) were crosslinked with different concentrations of aqueous ammonia solutions. As may be seen the higher the concentration of $NH_3$ used, the higher the percentage of undissolved SCPE in the sample. Fig. 2 shows a comparison of the weight percent of undissolved SCPE (B50) when cured in a 20.0% $NH_3$ solution at room temperature and at more extreme conditions. It is seen that the highest degree of crosslinking was achieved when fractionated SCPE was crosslinked at 50°C and postcured at 100°C. When blended with PVC, SCPE (B50) was crosslinked under the same conditions yielding 35% of undissolved weight.

Ammonia solution did not proved to be an efficient crosslinking agent for B40 and B50. In order to achieve an appreciable degree of crosslinking , it was necessary to employ extreme conditions such as the use of fractionated SCPE in

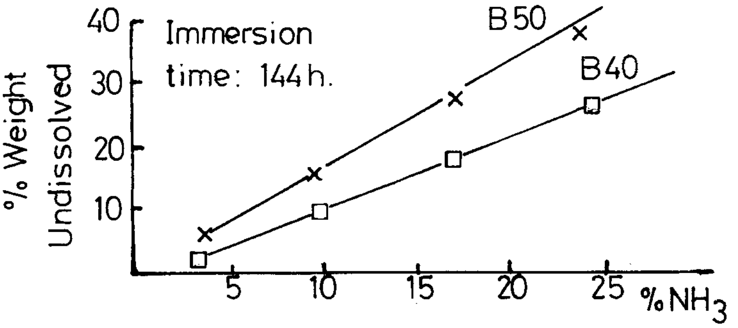

FIGURE 1. Percentage weight of undissolved B40 and B50 cured with ammonia vs. ammonia conc.

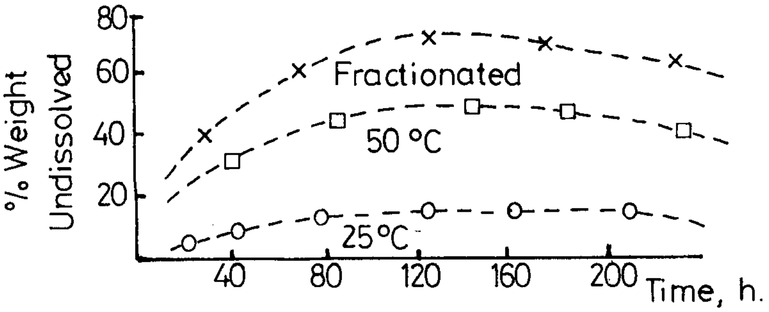

FIGURE 2. Percentage weight of undissolved B50 crosslinked with a 20.0% of $NH_3$ in solution.

the blend and immersion of the sample for long periods in the curing media at 50°C, followed by postcuring between 75° to 100°C. Fractionation of SCPE prior to curing increased crosslinking because the smaller chains in the polymer were removed; if present, these chains may have formed branches on larger molecules reducing the number of sites available for crosslinking. The use of curing temperatures above ambient, was necessary since the crosslinking reaction depends on the rates of diffusion and reaction of ammonia in the sample and the degree of crosslinking is a function of the final concentration of ammonia, in the sample and increases with temperature. By postcuring, the remaining ammonia in SCPE was allowed to react thus increasing the degree of crosslinking. The drop in weight of undissolved SCPE observed in figure 2 after the sample was immersed for 144 h in ammonia solution is probably due to the hydrolysis of some sulphonamide crosslinks caused by the alkaline ammoniacal conditions. This side reaction would give a rise to an ammonium sulphonate salt.

As already mentioned SCPE crosslinked less efficiently after being blended with PVC. This suggests that the presence of PVC, which has a $T_g$ 63° higher than that of SCPE decreases the diffusion rate of $NH_4OH$ in the polymer, therefore influences the final concentration of this curing agent and the degree of crosslinking.

It is interesting to point out that after crosslinking one of the polymers in the blend, the resulting product may be classified[5,6] as a semi-IPN. This classification is applicable to the blends studied in this work (B40 and B50).

## CONCLUSIONS

In this paper, the effect of ammonia solution as a crosslinking agent for sulphochlorinated polyethylene (SCPE) before and after being blended with polyvinyl chloride (PVC) is examined. SCPE, with 50%Cl content and 1% S as $SO_2Cl$ groups, was prepared by an extension of the chlorosulphonation reaction of small molecules known as the Reed reaction. SCPE/PVC blends with 40 and 50% w/w of SCPE were prepared by solvent casting. Before and after blending, the SCPEs were crosslinked by immersing them in different concentrations of ammonia solution (5.0, 20.0, 30.0 and 35% $NH_3$) at room temperature for one week.

The degree of crosslinking of the cured samples before and after blending were determined by swelling measurements. It was seen that the higher the concentration of $NH_3$ used, the higher the percentage of undissolved SCPE in the sample. The crosslinking efficiency for the blends was poor, suggesting that the presence of PVC decreases the diffusion rate of $NH_4OH$ in the polymer. The sudden change from single phase to partially miscibility makes the study of the effect of crosslinking in these systems very complex. Nevertheless the present results prove that an appreciable degree of crosslinking in the blend requires the employment of extreme conditions such as the use of fractionated SCPE and immersion of the blend sample for long periods in the curing media.

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