Preparation of Crosslinked and Thermostable Paste Poly(vinyl chloride)

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ABSTRACT: The grafting of a mercaptoalkyltrialkoxysilane onto an activated poly(vinyl chloride)(PVC) paste resin with subsequent hydrolytic crosslinking has been studied. The resins were prepared by copolymerization of vinyl chloride monomer and glycidyl-methacrylate(GMA). The grafting of a mercaptosilane was carried out during gelation of the plastisol. In this step the formation of a chemical network was avoided. By steaming at 120°C for 30 min the grafted samples crosslinked. The gel yield increased with increasing fraction of GMA and up to a given level with the fraction of the mercaptosilane. When using a resin of PVC homopolymer no crosslinking occurred. The silane grafted and crosslinked samples were found to have satisfactory thermal stability. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67**: 849–853, 1998

Key words: activated poly(vinyl chloride); paste PVC; hydrolytic crosslinking; PVC/GMA copolymer; mercaptosilane grafting

INTRODUCTION

Flexible PVC is one of the most versatile plastic materials in the world today. However, the material has some limitations. The most serious ones are the moderate upper service temperature limit and the limited resistance to solvents. To extend the application range it is possible to introduce a permanent chemical network.

This may, for instance, be done by crosslinking the PVC resin in the presence of a reactive plasticizer.[1–9] The most commonly used "plasticizers" are di- or tri-functional acrylates or methacrylates. Such compounds will, in the presence of irradiation[1–6] or free radicals,[8,9] rapidly homopolymerize followed by grafting onto the PVC backbone. So far irradiation is the only process that seems to have reached some commercial importance.

Alternatively, difunctional nucleophiles have been used to introduce crosslinks. The use of dithioltriazines were first described by Mori and Nakamura.[10] A strong nucleophile was prepared by transforming the mercapto functionality to thiolate anion by the aid of a metal salt. The grafting onto the PVC backbone takes place by nucleophilic attack on the polarized carbon–chlorine bond. Since heat is needed to facilitate the reaction this technique has some limitations. Crosslinking can hardly be separated from the processing step and the melt viscosity will be too high for standard PVC processes like extrusion and calendering.

Silane crosslinking of polyolefins is well known and is a commercially established process. This method has a number of advantages compared to peroxide and radiation crosslinking.[11] The process involves grafting of a silane group onto the polymer backbone, either during polymerization[12] or mechanochemically[13] with the help of peroxides during the processing operation, or by covalently coupling of an organofunctional silane. The polymer crosslinking is subsequently effected at a postfabrication stage by hydrolysis and condensa-

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tion. Crosslinking of PVC by similar methods has also been reported.[14-19] However, in the case of PVC the process has not been applied commercially to any extent. This is probably due to problems with premature crosslinking, inefficient grafting to the backbone, or strong degradation of the PVC. Nucleophilic reagents that have a strong basic nature often leads to degradation of the PVC backbone instead of nucleophilic substitution. Especially at high reaction temperatures where normal degradation of PVC starts to be of significance, it is important to make careful selection of both grafting reagents and processing conditions. Aminosilanes generally suffer from the weakness that they are too aggressive and thereby reduce the thermal stability of the PVC resin. Other works describe the use of less aggressive mercaptosilanes on halogenated polymers. However, without the presence of further additives, organic amino compounds,[20-22] or organic compounds of cadmium,[23] extensive processing conditions must be applied to achieve grafting with subsequent crosslinking. The addition of "activators" has a disadvantage since they increase the sensitivity of the polymer to degradation.

The present work is also a crosslinking process using a mercaptosilane. In order to solve the problem with inefficient grafting at mild preparation conditions, a reactive group has been introduced on the polymer backbone. Such a group could serve as the site for anchoring the crosslinking agent. This method of increasing the grafting efficiency on PVC backbones was first reported in a Norwegian patent[24] and applications in suspension PVC grades have been presented.[25] The aim of the present work is therefore to extend this activated resin technology to also be successful for a crosslinkable paste PVC. It is of interest to characterize the activated paste PVC and describe its behavior in an ordinary plastisol process where the plastification is different from suspension grades in that the resin only needs thermal heat treatment.

EXPERIMENTAL

Materials and Sample Preparation

The poly(vinyl chloride) (PVC) resins were prepared by homopolymerization of vinyl chloride monomer (VCM) (Norsk Hydro), or copolymerization of VCM with glycidylmethacrylate (GMA) (Rôhm GmbH), in a minisuspension polymeriza-

Table I   Plastisol Formulations

Chemicals/Materials	Formulation (phr)
PVC resin	100
DOP	60
Irgastab TK262GV	2
Dynasylan 3201	0–5

tion process[26] producing latexes with a mean volume particle diameter in the area 0.9–1.0 μm. By adjusting the amount of GMA added (1–3 wt % of total monomer) in the polymerization step the number of reactive epoxy sites in the resin was easily adjustable. The latexes were dried in a laboratory dryer and ground to a free-flowing powder.

Di-octylphtalate plasticizer (DOP) (Jayflex DOP, Exxon), organotin stabilizer (Irgastab TK262GV, Ciba), and mercaptopropyltriethoxysilane (Dynasylan 3201, Dynamit Nobel) were used as received. The PVC plastisols were prepared according to formulations given in Table I. The concentrations are given per hundred of PVC-resin (phr). The mixture of the liquid ingredients were blended with the PVC resin in a Hobart mixer for 10 min. A smooth paste was obtained in each case. Plastisols were coated onto a release paper with a film thickness of 1 mm. The samples were fused in a Werner-Mathis oven for 5 min at given temperatures (190, 200, 210°C). Crosslinking was performed by steaming film samples at 120°C for 30 min at 1.2 bar. To study plastisol aging the plastisols were stored in a constant temperature and humidity room ($T = 23$°C, 50% RH) for 72 h.

Characterization

The plastisol viscosity was measured by a Brookfield RTV viscometer at 2.5 (spindle 3), 10, and 50 rpm (spindle 6) after storage for 1 and 72 h in the constant environment room.

The thermal stability of the flexible films were measured by the yellowness index (YI) with a Dr. Lange Microcolorimeter after exposure to 200°C. YI was measured in intervals of 3 min up to a total time of 33 min.

The degree of crosslinking was measured by immersing samples in tetrahydrofuran (THF) (p.a. quality, Fluka) for 24 h and calculating the % gel as [(weight$_{after THF}$/weight$_{before THF}$) × 100%]. A 100% gel indicates that all polymer molecules and all mercaptosilane is included in a homogenous network. The liquid ingredients were not included in the calculated gel %.

Table II   Effect on Gel Content of Untreated and Steamed Samples Fused at Different Temperatures

PVC Resin (% GMA)	Dynasylan (phr)	Gel Content (%)					
		190°C		200°C		210°C	
		—	Steam	—	Steam	—	Steam
0	0	—	—	—	—	—	—
0	1	—	—	—	—	—	—
0	3	—	—	—	—	—	—
0	5	—	—	—	—	—	—
1	1	—	—	—	37	—	46
1	3	—	—	—	49	—	82
1	5	—	—	—	52	—	73
3	1	—	49	—	64	—	58
3	3	—	62	—	65	—	69
3	5	—	56	—	63	—	65

RESULTS AND DISCUSSION

Table II shows gel contents of samples fused at different temperatures before and after steaming. It is seen that the reactivity of the resin is easily adjusted by the amount of GMA. With no GMA on the backbone (homopolymer) no crosslinking occurs, showing that no anchoring of the mercaptosilane with subsequent crosslinking has taken place. Crosslinking before steaming the samples has also been avoided, showing that the silane functionality is not activated during the processing step. All kinds of products can thus be manufactured without crosslinking taking place. By the end of processing, crosslinking may be activated under water or humid conditions. The results in Table II also indicate that the amount of crosslinks formed levels out with increasing amounts of silane compound, showing that it is the amount of reactive sites on the backbone, which is decisive for the achievable level of crosslinking. An excess amount of silane does not increase this. In addition, the results show that without including an active group on the PVC backbone, the mercaptosilanes will not be grafted under the given processing conditions.

There is no increase in gel content at the highest GMA level when the film is fused at the highest temperature, i.e., 210°C. This may be due to the different side reactions that occur. Lactone formation has earlier been described.[27] The glycidyl ester is then released as epichlorhydrin and the ester group forms a lactone ring structure on the backbone (see Fig. 1). The epoxy group is then no longer available as an anchoring point for the mercaptosilane grafting reaction. The reduction in degree of crosslinking may also be due to hydrochloric acid released by PVC degradation adding to the epoxy groups, and thereby reducing the number of grafting points.

The plastisol viscosity is given in Figure 2 for a resin of homopolymer and for a copolymer resin with 3 phr GMA. There is a small increase in viscosity with increasing level of GMA. From Figure 3 it is also seen that the viscosity aging is greater for the GMA copolymer resins. This is probably due to the plasticizer having a higher degree of interaction with the copolymer and by that more plasticizer is absorbed into the copolymer resin, i.e., the plastisol viscosity increases.

In addition to being a crosslinking agent the mercaptosilane also works as a plasticizer. This is shown in Figure 2–4 where the plastisol viscosity decreases with increasing additions.

Thermostability, measured by the means of yellowness index (YI), of the samples, has been tested. Figure 5 shows the effect of mercaptosilane in samples prepared with resins containing 3 phr of GMA. Thermostability with different additions gives relatively equal results, indicating that mercaptosilane level has no or little effect on the thermal stability of the films when gelled at 200°C. The thermostability of an activated resin
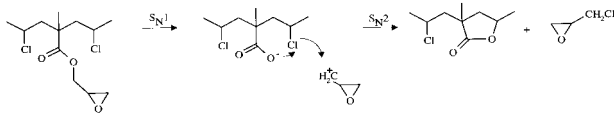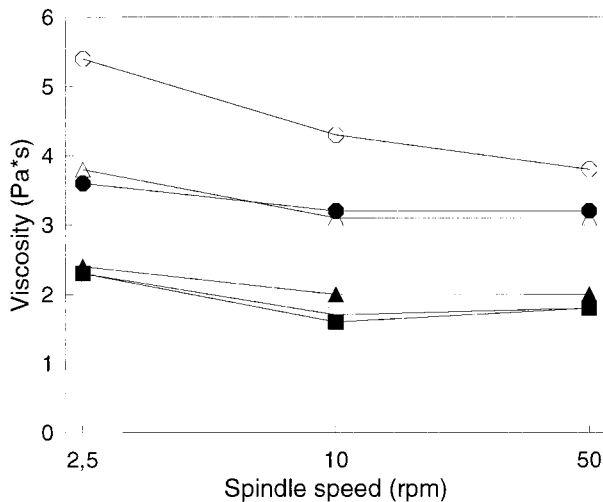

Figure 1   Lactone formation.

Figure 2 Plastisol viscosities for a resin of homopolymer (HP) and for a 3 phr GMA copolymer resin (CP), with different concentrations of mercaptopropyltriethoxysilane (DS). (●) HP with 1 phr DS; (▲) HP with 3 phr DS; (■) HP with 5 phr DS; (○) CP with 1 phr DS; (△) CP with 3 phr DS; (□) CP with 5 phr DS.

and the homopolymer are also comparable. The problems occurring when applying additional activators and rough processing conditions[14–19] are therefore avoided. The effect of gelling temperature and amount of mercaptosilane on YI are given in Figure 6. It is seen that increased amount
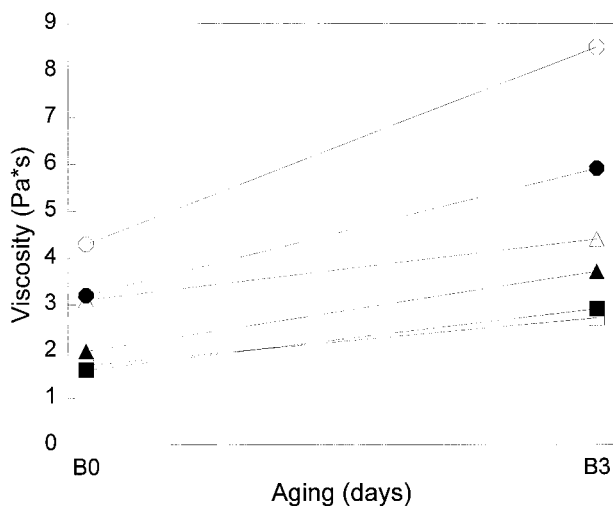

Figure 3 Viscosity aging measured as viscosity after mixing and after 3 days for a resin of homopolymer (HP) and for a 3 phr GMA copolymer resin (CP), with different concentrations of mercaptopropyltriethoxysilane (DS). (●) HP with 1 phr DS; (▲) HP with 3 phr DS; (■) HP with 5 phr DS; (○) CP with 1 phr DS; (△) CP with 3 phr DS; (□) CP with 5 phr DS.
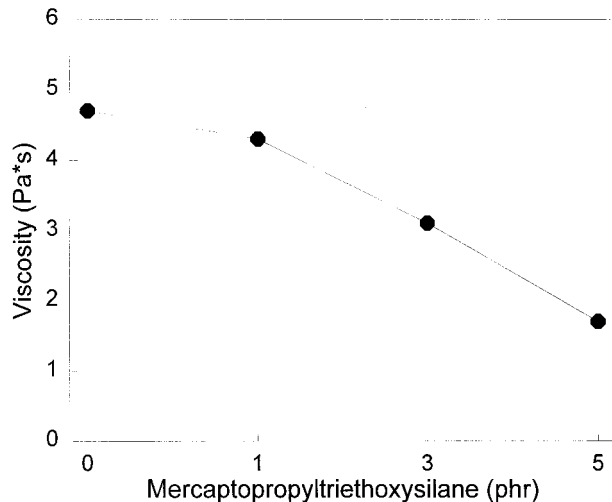

Figure 4 Effect of mercaptopropyltriethoxysilane concentration on viscosity with 3 phr GMA copolymer resin. Spindle speed: 10 rpm.

of the silane gives more yellowing when gelled at 210°C. This indicates that at the highest fusing temperature, degradation reactions have become noticeable.

Another explanation for the decreased stability may be due to the carbonyl oxygen in the methacrylate ester forming hydrogen bonds to hydrogen on the PVC chain and thereby increasing the rate of dehydrochlorination. However, since the copolymer resin in the absence of mercaptosilane only shows a small decrease in stability, the main reason for decreased stability seems to be the effect
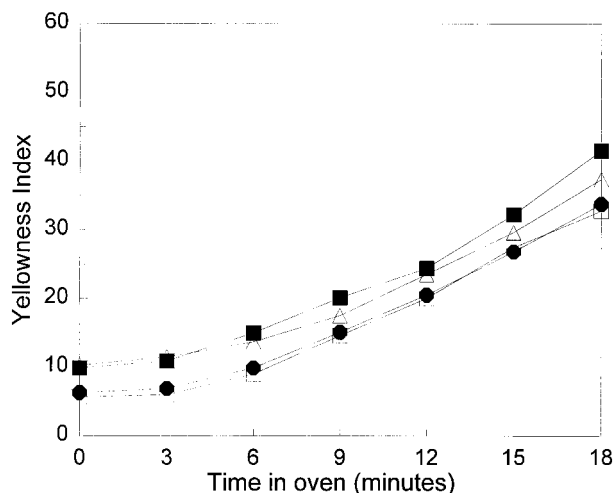

Figure 5 Effect of mercaptopropyltriethoxysilane (DS) concentration on yellowness index (YI) with 3 phr GMA copolymer resin. Gelation temperature: 200°C. (□) 0 phr DS; (■) 1 phr DS; (●) 3 phr DS; (△) 5 phr DS.
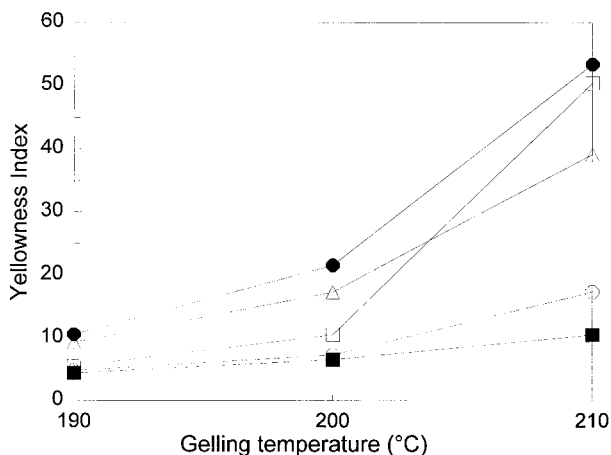
Figure 6 Effect of gelling temperature and mercapto-propyltriethoxysilane (DS) concentration on yellowness index (YI) with a homopolymer (HP) and with a 3 phr GMA copolymer (CP) resin. Time in oven: 5 min. (■) HP and 0 phr DS; (○) CP and 0 phr DS; (△) CP and 1 phr DS; (□) CP and 3 phr DS; (●) CP and 5 phr DS.

of nucleophilic attack on the PVC backbone, which is a competing reaction to grafting on the epoxy group.

CONCLUSIONS

It was found possible to graft mercaptopropyltrie-thoxysilane onto a paste poly(vinyl chloride)/glyci-dylmethacrylate copolymer during gelation of the plastisol. In this step the formation of a chemical network was avoided. By subsequent steaming, the grafted samples crosslinked. When using a resin of PVC homopolymer no grafting occurred, and therefore no crosslinking was obtained with hy-drolytic treatment of these samples. At moderate gelatination temperatures, the gel yield increased with increasing fraction of GMA in the copolymer and up to a given level with the fraction of the mercaptosilane. The silane grafted and crosslinked samples were found to have satisfactory thermal stability. Only at elevated gelation temperatures was the mercaptosilane found to give secondary reactions and thereby decrease the thermal stability of the product.

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