

Modification of Poly(vinyl Chloride). XXXIII. Novel Poly(vinyl Chloride) Foam Crosslinked with 6-Dibutylamino-1,3,5-triazine-2,4-dithiol

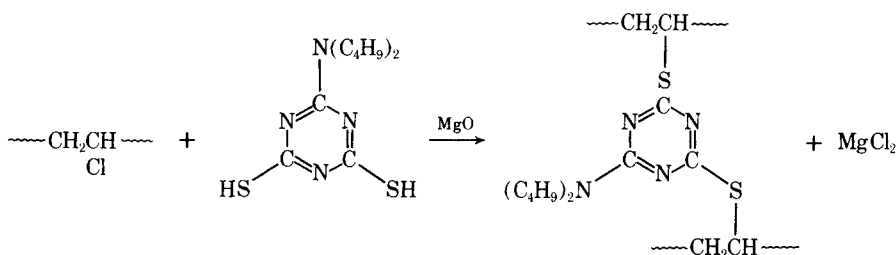
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Synopsis

The formulation for producing the PVC foam crosslinked with a novel crosslinking agent such as 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DB) was studied to determine the processing conditions. DB was almost consumed by radical combination with a coexistent blowing agent such as azobisformamide to give a high-density foam with excessively low crosslinking density. Blowing agents such as *p*-toluenesulfonylhydrazide (TSH) and 4,4'-oxybis(benzenesulfonylhydrazide) (OBSh) gave a crosslinked foam of low density, while a combination of the two crosslinking agents had moderate crosslinking reaction rate. The formulation recommended in the present study consists of PVC Zeon 101EP or Zeon 121 for paste, 100 parts; DOP, 100 parts; DB, 3–5 parts; OBSh or TSH, 10 parts; MgO, 1–3 parts; and RP101 (mixture of Ba, Ca, and Zn stearate), 2 parts, which gave colorless and insoluble foam of apparent density 0.14 under hot pressing at 180°C. The molded foam could be released without extraction of heat from a hot mold for fusion and expansion.

INTRODUCTION

Plastic foams are generally inferior to the original materials in resistance to solvents and dimensional stability at elevated temperatures. The crosslinking process may improve these defects to give a crosslinked foam with high expansion ratio by means of controlled viscosity of the molten polymer favorable for blowing. With this aim, a number of studies have been carried out on crosslinked PVC foam.¹ However, there is still great room for improvement in producing crosslinked PVC foam, because of the difficulty of the conventional crosslinking reaction for producing colorless foam and the unexplained details of this process in patents. In one of our earlier studies,² 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DB) has been found to react easily with PVC according to the following equation to give a crosslinked PVC having improved stability against discoloration:



Furthermore, the crosslinking reaction can be controlled with the acidity of a thiol group as well as the basicity of an acid acceptor added to the PVC blends.² In this paper, processing conditions and properties of the PVC foam crosslinked with a novel crosslinking agent such as DB are described.

EXPERIMENTAL

Materials

PVC (Zeon 101EP, average degree of polymerization $\bar{p} = 1450$; Zeon 121 for paste, $\bar{p} = 1650$) and blowing agents such as azobisformamide (ABFA, Unifor AC), *p*-toluenesulfonylhydrazide (TSH, Unifor H), and 4,4'-oxybis(benzenesulfonylhydrazide) (OBSh, Neocellubon) were supplied by Nippon Zeno Corp. and Eiwa Kasei Corp., respectively. Crosslinking agent 6-dibutylamino-1,3,5-triazine-2,4-dithiol (mp 142°–5°C) was supplied by Sankyo Kasei Corp. under the trade name of DB and was used without purification. Tricresyl phosphate (TCP), dioctyl phthalate (DOP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), and dioctyl sebacate (DOS) were used as plasticizers. A mixture of Ba, Ca, and Zn stearate (RP101, Tokyo Fine Chem. Corp.) was used as stabilizer against discoloration at elevated temperatures. All these additives were commercial products.

Method of Blending and Blowing

Procedure A. PVC Zeon 101EP, blowing agent OBSh, and additives as shown in Table III were mixed in a two-roll mill at 130°–135°C for 8 min. The mixed sheets were set in an oversized mold and allowed to fuse under a pressure of approximately 100 kg/cm² at 180°C for 7 min. After the heating cycle, the pressure was quickly reduced to take out the expanded products without any cooling. The crosslinked PVC foam thus obtained was a closed-cell foam of very uniform expansion and was used for the determination of the mechanical properties. A crosslinked foam of high density was also obtained by allowing expansion in an air oven of 190°C under atmospheric pressure for 5–7 min.

Procedure B. Plastisol obtained with PVC Zeon 121, blowing agent TSH, and additives as shown in Figures 1 and 3 and Table III charged into a stainless-steel mold about 0.25 mm thick and allowed to fuse at 110°C for 10 min. The resulting sheets, about 0.3 mm thick, were further heated in an air oven of 190°C to decompose the blowing agent under atmospheric pressure for 7–10 min to obtain a crosslinked PVC foam which was used to examine the processing conditions.

Determination and Instruments

Gas evolution data were obtained at an indicated temperature using 1 ml of 5% solution of the blowing agent in plasticizer with or without some ingredients of the PVC formulation. The gas evolved and measured in a Hempel gas buret according to the method of Hunter.³

The crosslinked PVC foams were extracted with tetrahydrofuran (THF) in a Soxhlet apparatus overnight. The remaining swollen gel was dried by vacuum

TABLE I
Total Gas Yield from Some Blowing Agents in DOP

Additive, 100 mg	Gas yield, ml/100 mg blowing agent, at 25°C, 1 atm		
	ABFA ^a	OBSh ^b	TSH ^c
None	26.6	14.6	11.3
DB	10.4	14.4	12.6
<i>t</i> -BHQ ^d	8.5	13.9	12.0
DB + MgO	14.0	13.2	10.5
DB-Na ^e	9.1	12.7	13.0

^a Heating temperature 200°C.

^b Heating temperature 155°C.

^c Heating temperature 150°C.

^d *t*-Butylhydroquinone.

^e 6-Dibutylamino-1,3,5-triazine-2,4-dithiol monosodium salt.

pumping in a desiccator at 60°C for at least 20 hr. The percentage of THF-insoluble material (gel-%) is given from the ratio of the weight of the dried gel and the weight of PVC in the initial sample.

The crosslinking behavior of the PVC compound was followed with an oscillating disk rheometer. The torque value indicated in cure-time curves is a function of the degree of crosslinking and the shear force which is in direct relationship to the hot-melt viscosity of the sample. The rate constant (k , min⁻¹) of the crosslinking reaction was calculated according to the equation described before.²

The mechanical properties of the crosslinked PVC foam were determined with a recording autograph P100 at an extension rate of 5 mm/min at 20°C. The zero-strength temperature was measured with a Tokyo Seiki tensile heat distortion apparatus (ASTM D1637-591) under the specified stress of 1.5 kg/cm² at a heating rate of 2°C/min. Permanent compression set was measured according to ASTM D395 Method B.

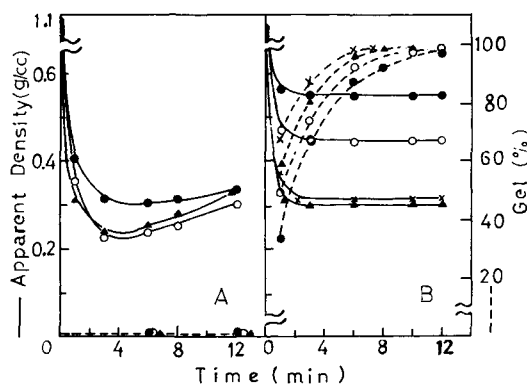


Fig. 1. Effect of processing temperature on apparent density and gel content of the pvc foam: (●) 170°C; (○) 180°C; (▲) 190°C, (×) 200°C. Formulation A: Zeon 121, 100 phr; DOP, 100 phr; RP101, 2 phr; TSH, 10 phr. Formulation B: Zeon 121, 100 phr; DOP, 100 phr; RP101, 2 phr; TSH, 10 phr; MgO, 3 phr; DB, 3 phr.

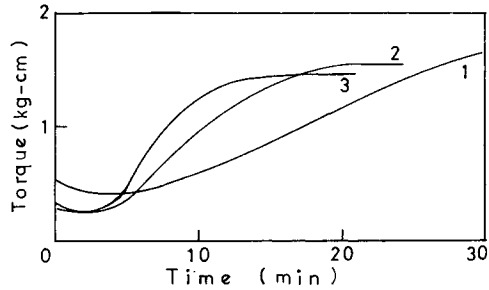


Fig. 2. Cure-time curves of PVC crosslinking formulation: (1) 180°C; (2) 190°C; (3) 200°C. Formulation: Zeon 121, 100 phr; DOP, 100 phr; MgO, 3 phr; DB, 5 phr; RP101, 2 phr.

RESULTS AND DISCUSSION

Blowing Agent

To compare the efficiency of some commercial blowing agents, the total gas yields were determined in dioctyl phthalate (DOP) containing some ingredients of PVC crosslinking formulation. Typical results obtained at each optimum heating temperature are shown in Table I. The total gas volume evolved from ABFA was found to be largely decreased in the copresence of crosslinking agent DB, which had been confirmed to readily accept the 1,1-diphenyl-2-picrylhydrazyl free radical.⁴

A similar decreasing effect on gas yield was also observed with *tert*-butylhydroquinone, which is known as an effective radical acceptor. Accordingly, DB would be almost consumed via radical combination with the fragments of coexistent ABFA to give a higher-density PVC foam with too low a crosslinking density. Hydrazides such as TSH and OBSH have been recommended in a re-

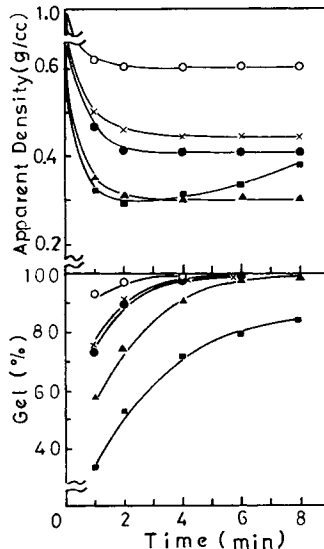


Fig. 3. Effect of rate of gel formation on apparent density of PVC foam at 190°C. (○) Composition A, disodium salt of DB, 4 phr; polyoxyethylene-23-lauryl ether (Brij 35), 2 phr; TSH, 10 phr. (×) Composition A, DB, 3 phr; Brij 35, 2 phr; TSH, 10, 10 phr. (●) Composition A, DB, 3 phr; Brij 35, 2 phr; OBSH, 10 phr. (▲) Composition A, DB, 3 phr; TSH, 10 phr. (■) Composition A, DB, 1 phr; TSH, 10 phr. Composition A: Zeon 121, 100 phr; DOP, 100 phr; RP101, 1 phr; MgO, 3 phr.

TABLE II
Effects of Properties of Plasticizer on Production of Crosslinked PVC Foam

Plasticizer	Fusion temperature, ^a °C	Crosslinking rate constant, ^b <i>k</i> , min ⁻¹ (180°C)	Gas yield, ml/100 mg TSH (at 25°C, 1 atm)	Apparent density, ^c g/cc
DBP	62	0.107	5.6	0.24
BBP	69	0.133	4.0	0.29
DOP	84	0.088	9.6	0.24
TCP	79	0.120	5.6	0.31
DOS	125	0.088	8.7	0.62

^a *Encyclopedia of Polymer Science and Technology*, Vol. 10, Wiley, New York, 1969, p. 247.

^b Zeon 101EP, 100 parts; plasticizer, 40 parts; MgO, 5 parts; DB 2.7 parts.

^c Zeon 121, 100 parts; plasticizer, 100 parts; MgO, 5 parts; DB, 3 parts; RP101, 2 parts; Brij-35, 2 parts; TSH, 10 parts; 190°C, 7 min.

cent study for making a low-density foam with a higher crosslinking density, since they were hardly affected by the coexistence of crosslinking agents such as DB to give nearly quantitative gas yield, as shown in Table I.

Processing Conditions

Temperature. The PVC formulation without crosslinking agent yielded foam products having similar densities at heating temperatures 170°–190°C, that is, high enough to produce complete fusion of the PVC, Figure 1(A). Furthermore, the density tends to increase again under a prolonged heating through a breakdown of the uncrosslinked cellular structure. The formulation using a

TABLE III
Typical Formulations and Properties of Crosslinked PVC Foam

Formulation, parts	Procedure A	Procedure B
PVC	Zeon 101EP, 100	Zeon 121, 100
DOP	100	100
DB	5	3
Blowing agent	OBSH, 10	TSH, 10
MgO	3	1
RP101 ^a	2	2
Brij 35 ^b	—	2
Properties	Procedure A	Procedure B
Hardness, rubber type F	58 (65) ^c	65 (67) ^c
Apparent density, g/cc	0.142 (0.30)	0.301 (0.395)
Gel, %	97 (0)	96 (0)
Tensile strength, kg/cm ²	11.3 (12.4)	8.2 (8.8)
Elongation at break, %	220 (233)	145 (173)
Permanent set (70°C × 22 hr × 40% compression), %	41.3 (56.7)	33.4 (45.3)
Zero-strength temperature (1.5 kg/cm ²), C°	146 (103)	123 (84)
Elongation at zero-strength temperature, %	180 (282)	213 (300)

^a Mixture of Ba, Ca, and Zn stearate.

^b Crosslinking accelerator, polyoxyethylene-23-lauryl ether.

^c Values in parentheses are the results on the PVC foams via procedure A or B without crosslinking agent (DB).

crosslinking agent, however, gives an insoluble and a lower-density foam, Figure 1(B), only under a high temperature of about 190°C, enough to decrease a hot-melt viscosity (torque value in Fig. 2) which tends to increase with increasing crosslinking. Above 190°C, expansion of the foam might be arrested by the rapid decrease of viscosity through a rapid formation of crosslinking structure to afford a slightly higher-density foam than at 190°C.

Crosslinking Agent. The crosslinking reaction rate of the PVC compound determines the density of the final foam product (Fig. 3). Under a similar processing temperature (190°C), the formulation with a moderate crosslinking rate tends to yield a low-density foam. When the rate (gel formation) is too high, the hot-melt viscosity must become high enough to prevent expansion of the foam to give a high-density foam. When the rate is too slow, then a breakdown of the foam structure followed by increase in density takes place in the fused composition with an excessively low hot-melt viscosity.

Since the amount of crosslinking agent as well as accelerator such as polyoxyethylene-23-lauryl ether is a function of the cross-linking rate, high-density foams were generally obtained with the formulations containing accelerator and a large amount of crosslinking agent (Fig. 3). Both TSH and OSH are effective for the production of low-density foams with a high crosslinking density.

Plasticizer. The density of the crosslinked PVC foam also depends on the kind of plasticizer as ingredient of the formulation. As shown in Table II, the effects of the kind of plasticizer are observed not only on crosslinking rate but also on the ease of fusion of the PVC-plasticizer blend, which were already shown to affect greatly the density of the foam. Furthermore, the gas yield evolved from the solution of TSH in each plasticizer is extremely affected by the kind of plasticizer. TCP, which accelerates the crosslinking reaction, and DOS, which has a higher fusion temperature, tend to produce foam products of high density. DOP and DBP are the most favorable plasticizers for the production of crosslinked PVC foams of lower density.

Properties

Some typical formulations recommended in the present study to produce a crosslinked PVC foam and the properties of the resulting foam are given in Table III. The values can be varied according to the amount of the blowing agent in the formulation. Although the mechanical properties under room temperature are hardly improved compared with those of the uncrosslinked foam, zero-strength temperature, compression set value, and dimensional stability at elevated temperatures can be much improved by crosslinking. Furthermore, the crosslinked foam has an excellent stability against discoloration at elevated temperatures. Accordingly, the novel crosslinking technique in this study could be applied to the manufactures of upholstery and underlays.

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