Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Application of Dithlol-s-triazine Derivatives to PVC CrossUnking

Yoshiro Nakamura[a]; Kunio Mori[a]
[a] Department of Applied Chemistry Faculty of Engineering, Iwate University, Morioka, Japan

To cite this Article Nakamura, Yoshiro and Mori, Kunio(1978) 'Application of Dithlol-s-triazine Derivatives to PVC CrossUnking', Journal of Macromolecular Science, Part A, 12: 2, 209 — 223

To link to this Article: DOI: 10.1080/00222337808061370

URL: http://dx.doi.org/10.1080/00222337808061370

J. MACROMOL. SCI.–CHEM., A12(2), pp. 209-223 (1978)

Application of Dithiol-s-triazine Derivatives to PVC Crosslinking

YOSHIRO NAKAMURA and KUNIO MORI

Department of Applied Chemistry
Faculty of Engineering, Iwate University
Morioka, Japan 020

ABSTRACT

The effects of crosslinking on PVC are well known in regard to the improvement of mechanical properties, creep behavior, and softening temperature. Little is known, however, on the application of the PVC-crosslinking reaction, because most of crosslinked PVC tends to color easily at elevated temperatures. In this paper, a novel PVC-crosslinking reaction with 2-R-4,6-dithiol-s-triazine (I) has been presented to obtain insoluble products which hardly color on ageing. The reaction rate and induction period of the crosslinking reaction with I are made controllable by selecting the basicity of the substituent R of I as well as that of an acid acceptor in the blends. The utility of I as stabilizer as well as a crosslinking agent is also emphasized.

INTRODUCTION

The reactivity of the activated thiolate anions were studied in order to prepare the thioether [1] and crosslinking PVC containing a thioether structure [2]. Conventional thiols, such as ethanedithiol and xylylenedithiol, however, are rarely used as PVC-crosslinking agents, as they generate bad odors on the PVC-mixing roll at elevated temperature. In our laboratory, 2-R-4,6-dithiol-s-triazine compounds (I), which are odorless and are reagents known to minimize pollution by toxic cations [3], were found to be effective crosslinking agents for such chlorine-containing rubbers as polyepichlorohydrin [4]. When PVC is crosslinked with I as in the present studies, the products, compared with the original PVC, have been found to show higher thermal stability for coloring. Although a number of PVC-crosslinking methods have been presented in the literature, little is known of commercial application of the PVC-crosslinking reaction. The reason appears to be mainly the decrease of thermal stability (coloration of aging) of the resultant products at elevated temperatures. The object of this paper is to present a new method for preparing thermally stable PVC crosslinked with I. The new method is based on the use of dithiol-s-triazines, which are excellent thermal stabilizers as well as an active crosslinking agents for PVC, and this lead us successfully to perform the present work.

EXPERIMENTAL

Model Reaction

A mixture of 27.2 g of 2-dibutylamino-4,6-dithiol-s-triazine, 10 g of magnesia, and 50 g of sec-C_4H_9Cl was heated in 200 ml autoclave at 180°C for 7 hr. The resulting product was extracted with 100 ml of methanol containing 1% zinc acetate, then the extracts were diluted with water. The diluted solution was extracted with ether, and the extracts were dried over anhydrous sodium sulfate to yield 34 g of 2-dibutylamino-4,6-dithiobutyl-s-triazine, yield 90.1%; mp 36-37°C.

ANAL. Calcd: S, 16.67%; N, 14.58%. Found: C, 16.3%; N, 14.7%.

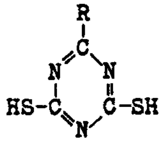
2-Substituted-4,6-dithiol-s-triazine (I)

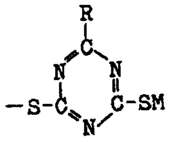
2-Substituted-4,6-dichloro-s-triazines which were prepared from cyanuric chloride by the methods of Thurston [5] were added to an aqueous or DMF solution of NaSH of triple the molar quantity. The mixture was stirred at 80°C until evolution of H_2S ceased, cooled, and neutralized with diluted HCl to yield I. Most of I are commercially produced today and supplied from Sankyo Kasei Co. (Kitaku Osakashi). Table 1 shows their properties.

Materials

PVC, plasticizer, I, and additives were obtained commercially and used without purification. Blended PVC sheets, about 0.5 mm

TABLE 1. Properties of 2-R-4,6-Dithiol-s-triazines





				Metal (%)	
R	Mp (°C)	R	Metal M	Found	Calcd
$N(C_2H_5)_2$	238-240	NHC_6H_5	Ba	36.3	36.93
$N(C_4H_9)_2$	138-140	"	Ca	27.7	14.6
$N(C_8H_{17})_2$	121-124	"	Zn	20.2	21.86
$NHCH_2C_6H_5$	179-181	$N(C_4H_9)_2$	Ba	33.9	33.72
NHC_6H_5	248-251	"	Ca	10.2	12.93
$N(C_6H_5)_2$	235-236	"	Zn	17.9	19.49

thick, were heated or compression-molded under 50 kg/cm^2 at 180°C for 5-20 min, and the crosslinked products were taken out without any cooling.

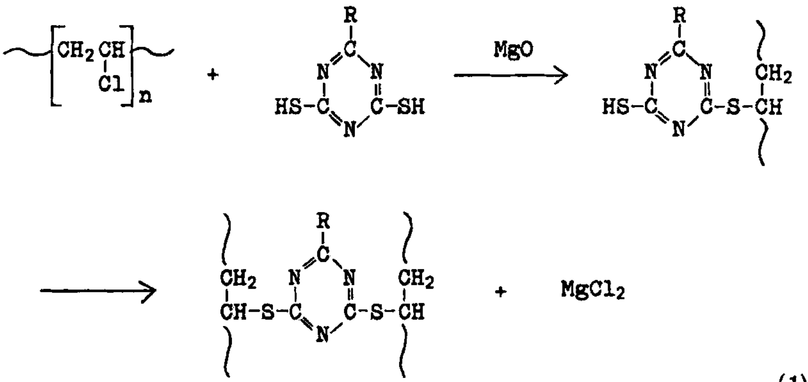
Methods of Blending and Analysis

The crosslinking reaction rate was observed by the determination of THF-insoluble fraction (gel content) and swelling ratio of the resulting sheets heated at prescribed conditions. The rate was also determined with an oscillating disk rheometer.

RESULTS AND DISCUSSION

Model Reaction and Crosslinking Reaction

When 2-dibutylamino-4,6-dithiol-s-triazine was heated at 180°C with sec-alkyl chloride in the presence of an acid acceptor such as magnesia, 2-dibutylamino-4,6-dithiobutyl-s-triazine was obtained in high yield. Elementary analysis of the residual PVC-gel of THF extraction followed by methanol shows that the crosslinking reaction, dehydrochlorinated condensation of PVC with I, takes place as shown in Eq. (1)



(1)

Crosslinking Conditions

Effect of Acid Acceptor. The rate of crosslinking of PVC with I depends on the basicity of the acid acceptor in the blends and increases in the order of the basicity, e. g., $CaCO_3 < MgO < CaO < BaO < Na_2CO_3 < K_2CO_3$ (Fig. 1). In this case, ZnO, PbO, the lead stabilizer and tin stabilizer, which react with the thiol group of I

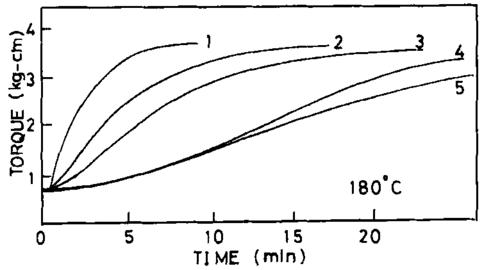


FIG. 1. Torque-time curves for PVC crosslinked with (1) K_2CO_3, k (180°C) = 3.28×10^{-1}; (2) Na_3CO_3, k = 1.53×10^{-1}; (3) BaO, k = 1.49×10^{-1}; (4) CaO, k = 0.94×10^{-1}; (5) MgO, k = 0.55×10^{-1}. Geon 101 EP, 100 parts; DOP, 40 phr; DB, 2.7 phr; Ca-Ba-Zn stabilizer (RP 101), 2 phr; acid-acceptor, 0.05 mole. DB = 2-dibutylamino-4,6-dithiol-s-triazine.

TABLE 2. Effect of MgO or DB salt on Rate of the Crosslinking Reaction[a]

Crosslinking agent (phr)			Reaction rate at 180°C
DB	DB salt	MgO (phr)	(min^{-1} × 10)
2.7	-	0	0.406
2.7	-	2	0.52
2.7	-	5	0.83
2.7	-	10	1.13
-	DB-Ba 4	-	1.37
-	DB-Ca 3.1	-	0.77
-	DB-Mg 2.9	-	0.37
-	" "	2	0.55
-	" "	4	0.71
-	" "	8	0.87

[a] Geon 101EP, 100 parts; DOP, 40 phr; RP101, 2 phr; crosslinking agent 0.01 mole; magnesia indicated. DB: 2-dibutylamino-4,6-dithiol-s-triazine; RP101: Ca-Ba-Zn stabilizer.

to give metal salt, however, tend to decrease the crosslinking reactivity of I. PVC is also crosslinked with the salt of I, and the crosslinking rate increases in the order magnesium < calcium < barium salt. An acid acceptor such as magnesia also accelerates the crosslinking (Table 2).

Effect of Substituent R. The rate of PVC crosslinking is influenced by the pk_a of thiol group of I, and I with the lower pk_a tends to show the higher reactivity to PVC (Fig. 2). The pk_a is also significantly related to the property of the substituent (R) on the s-triazine nucleus, and the more basic R tends to give I having a higher crosslinking reactivity (Fig. 3). I with pk_a over 5, which is ineffective for PVC crosslinking, however, is found to show the practical reactivity to PVC in the presence of an activator (polyethyleneglycol derivatives) or a strong acid acceptor such as K_2CO_3, Na_2CO_3 (Table 3).

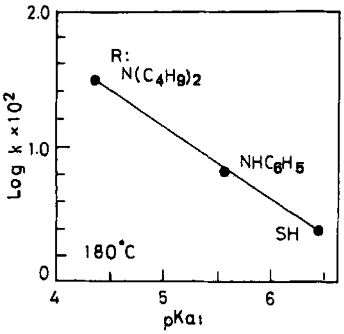


FIG. 2. Relation of pK_a of thiol group to crosslinking reaction rate. Geon 101 EP, 100 parts; DOP, 40 phr, K_2CO_3, 3 phr; 2-R-4,6-dithiol-s-triazine, 0.01 mole.

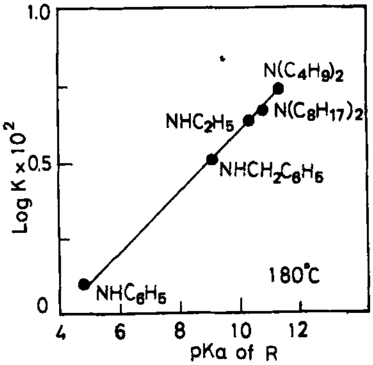


FIG. 3. Relation of the basicity of the substituent R of 2-R-4,6-dithiol-s-triazine to crosslinking reaction rate. Geon 101 EP, 100 parts; DOP, 40 phr; MgO, 5 phr; 2-R-4,6-dithiol-s-triazine, 0.01 mole.

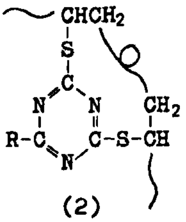
Effect of Plasticizer. The PVC crosslinking reaction is significantly influenced by the amount and the kind of the plasticizer in the blends. The reaction rate is higher with lower amount of plasticizer and with the plasticizer having a higher polarity, such as tricresyl phosphate. As shown in Figs. 4 and 5, the rate constant of PVC-crosslinking reaction was found to be proportional to the reciprocal of the dielectric constant of plasticizer. The equilibrium

TABLE 3. Effect of Activator of PVC Crosslinking[a]

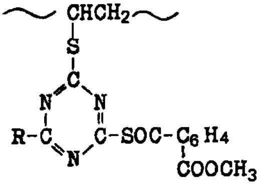
Crosslinking agent (phr)		Acid acceptor (phr)		Activator (phr)	Crosslinking rate at 180°C (min^{-1} × 10)	Induction period (min)
DB,	2.7	MgO,	2	-	0.55	4-5
"	"	"	"	5	1.03	
AF,	3.0	"	"	-	0.26	11-12
"	"	"	"	5	0.36	
TTCA,	2.0	"	"	-	0	
"	"	"	"	5	0.34	4
AF,	3.0	K_2CO_3,	3	-	0.57	7
"	"	"	"	5	1.78	0
TTCA,	2.0	"	"	-	0.25	10
"	"	"	"	5	0.94	5

[a] Geon 101EP, parts; DOP, 40 phr; RP101, 2 phr: crosslinking agent and acid acceptor as indicated. DB: 2-dibutylamino-4,6-dithiol-s-triazine; AF: 2-anilino-4,6-dithiol-s-triazine; TTCA: trithiocyanuric acid; activator: polyoxyethylene-23 lauryl ether (Brij 35).

swelling value of PVC crosslinked with an equal portion of I differs with the kind and amount of the plasticizer in the blends (Fig. 5 and Table 4). Nitrogen detected in the residual gel of THF-CH_3OH extraction, however, is approximately equal on the crosslinked PVC having different value of the equilibrium swelling, e. g., crosslinking density (Fig. 4 and Table 4). These results suggest that the reactions (2) and (3) which are ineffective in crosslinking, may occur besides the effective crosslinking reaction (1) in the presence of such plasticizers as butyl benzyl phthalate.



(2)



(3)

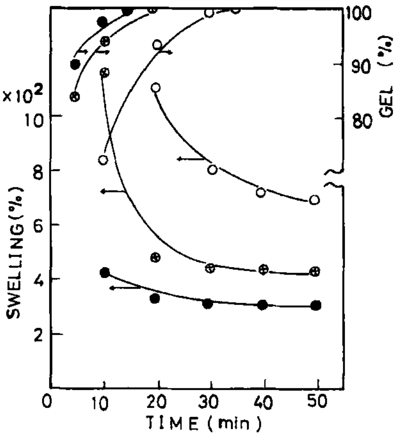


FIG. 4. Effect of the amount of plasticizer to equilibrium swelling ratio: (○) DOP = 70 phr, $\nu_e = 0.827 \times 10^{-4}$ mole/g, N = 0.83%; (⊗) DOP = 40 phr, $\nu_e = 2.39 \times 10^{-4}$ mole/g, N = 0.86%; (●) DOP = 10 phr, $\nu_e = 5.07 \times 10^{-4}$ mole/g, N = 0.85%. Geon 101 EP, 100 parts; DB, 5, phr; MgO, 5 phr, RP101, 2 phr; DOP variable. N (calcd.) = 0.93%.

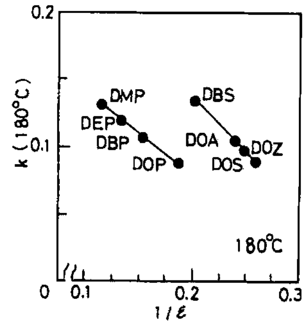


FIG. 5. Relation of dielectric constant ε of plasticizer to the crosslinking reaction rate. Geon 101 EP, 100 parts; plasticizer, 40 phr; MgO, 5 phr; DB, 2.7 phr.

TABLE 4. Effect of the Plasticizer on Equilibrium Crosslinking Density[a]

Plasticizer (40 phr)[b]	ν_e at equilibrium (mole × 10^4/g)	N (%)[c]
BBP	0.38	0.91
DMP	0.92	0.89
DBP	1.27	0.96
DOP	1.32	0.86
DOZ	1.36	0.92
DOA		0.89
DBS	1.19	0.97

[a] Geon 101EP 100, parts; plasticizer, 40 phr; MgO, 5, phr; DB, 2.72 phr.

[b] Plasticizers: BBP: butyl benzyl phthalate; DMP: dimethyl phthalate; DBP: dibutyl phthalate; DOP: dioctyl phthalate; DOZ: dioctyl azealate; DOA: dioctyl adipate; DBS: dibutyl sebacate.

[c] N% of the extracted gel of the crosslinked PVC obtained by 5 phr of DB; calcd. 0.97%.

Stabilizing Effect of I on Coloration

Coloration of PVC at elevated temperatures is well known to be inhibited by the Ba-Zn or Ca-Zn type stabilizers such as RP101, or Mark LC45. "Ba or Zn burning" caused by $BaCl_2$ and $ZnCl_2$ which are formed on aging is also known to be prevented by the addition of a chelating agent or magnesia. In the present study, I or alkali earth salts of I added as costabilizer or as crosslinking agent have been found to show an improved stabilizing ability in combination with magnesia or calcium oxide to give fairly stabilized PVC which is not colored for 80 min at 180 C. Addition of I can lengthen a thermal stability of PVC up to around twice that of conventional stabilizer (Table 5 and Fig. 6). As described above, I shows a different degree of reactivity to PVC, depending on the acidity of thiol group and the basicity of the coexistent acid acceptor. Accordingly, the formation of a longer polyene chain may be avoidable through use of compounds I which never react with the original chlorine atoms but tend to substitute such an activated chlorine (allylic chloride) that plays an

TABLE 5. Stabilizing Effect of Thiol-s-triazine on the Discoloration of Uncrosslinked PVC

	No. 1	No. 1'	No. 2	No. 2'	No. 3	No. 3'	No. 4	No. 4'	No. 5
Geon 101EP, parts	100	100	100	100	-	-	-	-	-
Geon 121, parts	-	-	-	-	100	100	100	100	-
DOP, phr	40	40	40	40	90	90	90	90	40
Dibutyltin maleate, phr	1	1	-	-	-	-	-	-	-
Dibutylthiotin glycolate, phr	-	-	1	1	-	-	-	-	-
Dibutyltin oxide, phr	-	-	-	-	0.5	0.5	-	-	-
MgO, phr	-	-	-	-	1	1	2	2	3
Barium stearate, phr	-	-	-	-	-	-	-	2	-
Ba-Ca-Zn stabilizer (RP101), phr	-	-	-	-	-	-	2	2	2
Thiol-s-triazine, phr	-	AF, 0.5	-	AF-Ca, 0.5	-	AF, 0.5	-	DB-Ba, 2	AF-Ca, 1

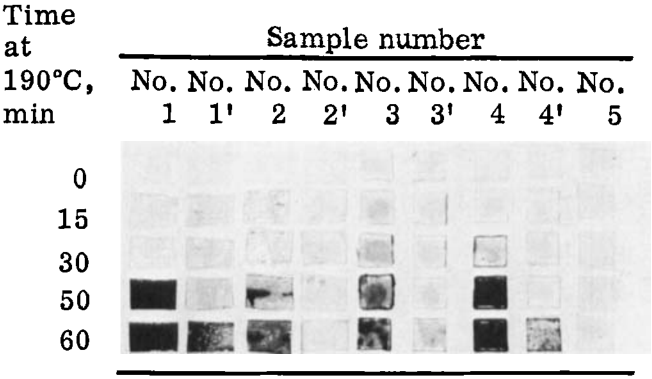


FIG. 6. Thermal stability of PVC samples. Recipes given in Table 5.

important role, serving as a trigger for zipperlike dehydrochlorination. Really, less reactive I compounds such as 2-anilino-4,6-dithiol-s-triazine (AF) which hardly reacts as a crosslinking agent on PVC has been confirmed to bond chemically with PVC to show a remarkable stabilizing effect for coloration. An excellent stabilizing system selected in this work, is the combination of AF or 2-diphenylamino-4,6-dithiol-s-triazine (DP) with alkaline earth oxide (MgO, CaO) and some stearates (Table 5). This system further inhibits the coloration in the presence of Ca, Ba, and Zn salt which show the property of complementary coloring [6]. The stabilizing effect of I for the coloration of PVC was confirmed to be based on a strong inhibitory action to zipperlike dehydrochlorination through the substitution of allylic chloride structure. On the basis of the radical-accepting reactivity of I with 1,1-diphenyl-2-picrylhydrazyl, I is assumed also to stabilize the free radical that accelerates the decomposition of PVC and thus inhibits the coloration. Such an action is not observed with the commonly used metal stearate. I may therefore be widely applicable as a nontoxic stabilizer without Cd and Pb. In addition, the stabilizing system with I was found to be distinctly effective on PVC blends with incombustible plasticizers such as tricresyl phosphate and substituted phenyl phosphate which are inferior to dioctyl phthalate in a color stability.

Application to PVC Processing and Properties of the Crosslinked Products

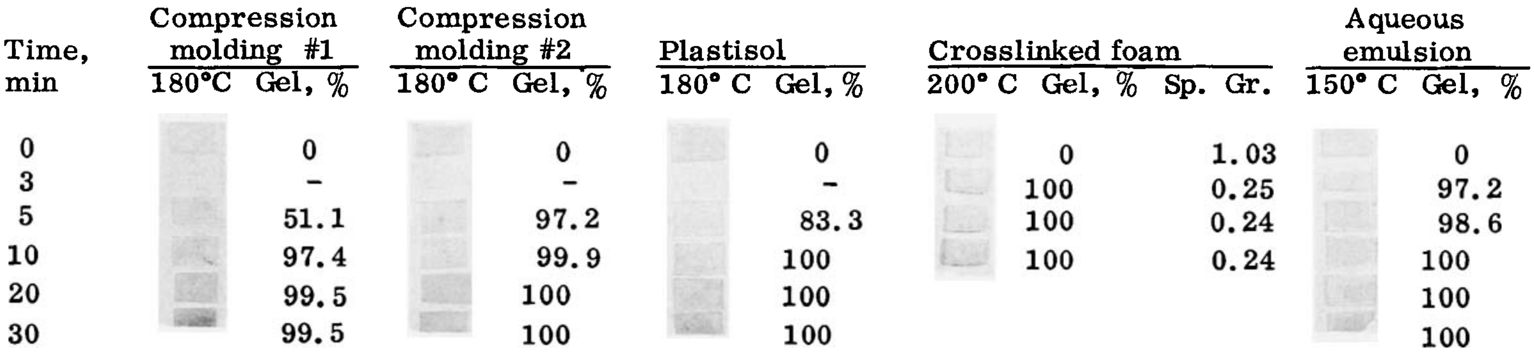
As described above, I has been found to react quantitatively with PVC to form crosslinked products which are hardly discolored on aging for 30-60 min at 180°C. This reaction has consequently been

TABLE 6. Application to PVC Processing

	Compression molding #1	Compression molding #2	Plastisol	Crosslinked foam	Aqueous emulsion
PVC type (100 parts)	Geon 101 EP	Geon 101 EP	Geon 121	Geon 121	Geon 576
DOP (phr)	40	40	90	100	-
Thiol-s-triazine (phr)[a]					
DB	3	-	-	3	-
DB-Ba	-	4	-	-	-
DB-Na or AF-Na	-	-	5	-	-
DB-2Na	-	-	-	-	2
Ca-Ba-Zn stabilizer (RP101) (phr)	3	2	-	2	-
MgO	3	4	3	5	-
Additives (phr)					
Barium stearate	-	2	-	-	-
Brij 35[b]	-	0.5	1.0	2.0	-
p-Toluene sulfonyl hydrazide	-	-	-	10	-

[a] DB: Dibutylamino-4,6-dithiol-s-triazine; AF: 2-anilino-4,6-dithiol-s-triazine.

[b] Brij 35: $CH_3(CH_2)_{11}O(CH_2CH_2O)_{23}H$.



Time, min	Compression molding #1 180°C	Compression molding #1 Gel, %	Compression molding #2 180° C	Compression molding #2 Gel, %	Plastisol 180° C	Plastisol Gel, %	Crosslinked foam 200° C	Crosslinked foam Gel, %	Crosslinked foam Sp. Gr.	Aqueous emulsion 150° C	Aqueous emulsion Gel, %
0		0		0		0		0	1.03		0
3		–		–		–		100	0.25		97.2
5		51.1		97.2		83.3		100	0.24		98.6
10		97.4		99.9		100		100	0.24		100
20		99.5		100		100					100
30		99.5		100		100					100

FIG. 7. Application of PVC crosslinking reaction to commercial samples. Recipes given in Table 6.

employed in compression-molding, foams, plastisol, and aqueous emulsion processing to prepare the crosslinked PVC. Typical compositions and results are shown in Table 6 and Fig. 7, respectively.

Compression Molding. The experimental compositions as described in Table 6 were blended in a two-roller mill with heating at 150-160°C for 5-10 min. The blended sheets, about 0.5 mm thick, are colorless and soluble in tetrahydrofuran. These were compression-molded in a press under a pressure of about 50 kg/cm^2 at 180°C for 5-20 min. The colorless crosslinked PVC sheet about 1 mm thick was taken out without any cooling. The properties of the resulting products are shown in Figs. 8 and 9. .Higher tensile strength and lower permanent tension set are observed at optimum crosslinking density (0.1-0.2 mole × 10^{-4}/g). The mechanical properties at elevated temperatures are also remarkably improved by crosslinking, compared with the uncrosslinked product.

Plastisol Processing. The plastisol compositions described in Table 6 were poured into a stainless mold, degassed under reduced pressure, then heated to fuse in air oven at 180°C. A crosslinking reaction occurs within few minutes with the alkali metal salt of DB [7]. The resulting sheets are insoluble in tetrahydrofuran, and remain colorless for more than 60 min at 180°C. The above processes yield flexible, infusible foams with the addition of blowing agent such as p-toluenesulfonyl hydrazide.

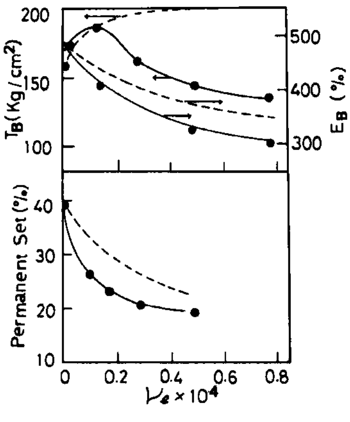


FIG. 8. Relation of mechanical properties and permanent set to crosslinking density (ν_e): (--) Geon 101 EP (100 parts) DOP (80 phr), MgO (5 phr), DB (4 phr), Ca-Ba-Zn stabilizer (RP 101) (2 phr); (—) same recipe with FEF carbon (20 phr).

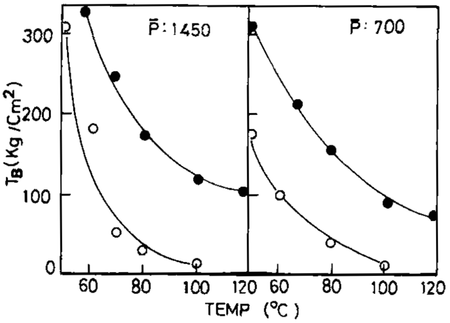


FIG. 9. Tensile strength of (o) uncrosslinked control and (●) the crosslinked PVC at elevated temperatures. Geon 101 EP or 103 EP8D 100, DOP 5, DB 4, MgO 5, RP 101 3 phr Crosslinked PVC with P = 1450 had $\nu_e = 0.617 \times 10^{-4}$ mole/g; PVC with P = 700 had $\nu_e = 0.889 \times 10^{-4}$ mole/g.

Processing of Aqueous PVC Emulsions. The mono- or disodium salt of 2-dibutylamino-4,6-dithiol-s-triazine, very soluble in aqueous PVC emulsion, can be employed in the active crosslinking agent for aqueous PVC emulsion. Aqueous PVC emulsion compositions (Table 6) were spread onto a glass plate and the prepared plate was placed in a forced draft oven of 50°C to dry. The dried film was then heated at 130-180°C to give THF-insoluble, colorless and transparent films (Fig. 7).

REFERENCES

[1] K. Mori and Y. Nakamura, Nippon Kagaku Kaishi, 1776 (1975).

[2] K. Mori and Y. Nakamura, Nippon Kagaku Kaishi, 2229 (1975).

[3] Y. Nakamura, Kagaku Kogyo, 16, 81 (1972); Ger. Pat. 2,240,549; U. S. Pat. 3,778,368 (1973).

[4] Y. Nakamura, Nippon Gomu Kyokaishi, 46, 779 (1973); Japan. Pat. 73-36926; U. S. Pat. 3,787,376.

[5] J. T. Thurston and F. C. Schaefer, J. Amer. Chem. Soc., 73, 2981 (1951).

[6] T. Iida and K. Goto, J. Appl. Polym. Sci., 19, 235, 243 (1975).

[7] Y. Nakamura, Angew. Makromol. Chem., 66, 169 (1978).